Cost and Performance Report

In Situ Anaerobic Bioremediation

Pinellas Northeast Site

Largo, Florida

Innovative Treatment
Remediation Demonstration

U.S. Department of Energy

April 1998

1. SUMMARY

In early 1997, the Innovative Treatment Remediation Demonstration (ITRD) Prog ram conducted a pilot study at the Pinellas STAR Center's Northeast Site to treat chlorinated volatile organic compounds (VOC) using *in situ* anaerobic bioremediation. The Northeast Site is characterized by VOC contamination of a shallow, sandy, surficial aquifer. Monitoring data indicate that some biodegradation of these contaminants is already occurring at the site. The primary objectives of this pilot study were to 1) evaluate the use of nutrient injection to enhance *in situ* anaerobic biological degradation rates of chlorinated VOCs in areas of moderate contaminant concentrations and 2) obtain operating and performance data to optimize the design and operation of a full-scale system. During the short operational period of this pilot study, there was no emphasis on reducing any contaminants to a specific regulatory level.

The pilot system was located in an area of the site that had total chlorinated contaminant concentrations in ground water generally ranging from 10-400 ppm, with one monitoring well having concentrations in excess of 2900 ppm. The bioremediation pilot system consisted of three 8-ft deep, gravel-filled, surface infiltration trenches and two 240-ft long horizontal wells with 30-ft screened intervals. The horizontal wells, directly underlying and parallel to the middle surface trench, were at 16- and 26-ft depths. The study area was about 45 feet by 45 feet and extended from the surface down thirty feet to a thick, clay confining layer 30 feet below the surface. Ground water was extracted from the upper horizontal well and recirculated via the surface trenches and lower horizontal well while benzoate, lactate, and methanol were added to the recirculated water to serve as nutrients for the dechlorinating bacteria. The nutrient concentrations were selected based on an earlier laboratory treatment study conducted through the ITRD Program. To assess hydraulic flow characteristics and nutrient delivery, a bromide tracer was added to the water reinjected through the deep horizontal well and an iodide tracer was added to the water fed to the surface trenches. VOC, tracer, and nutrient concentrations were monitored bi-weekly at 16 well clusters (each with 4 vertically discrete sampling intervals) spaced throughout the treatment area. VOC concentrations of the extracted ground water were also continuously monitored.

The system operated from February 7, 1997 to June 30, 1997. During this period, ground water was extracted and recirculated at a rate of about 1.5 gpm. Approximately 250,000 gallons of water, based on soil porosity of about two pore volumes, were circulated during the pilot study. Tracer and nutrient monitoring data indicated that nutrient were delivered to 90% of the central treatment area during operations. Wells not showing breakthrough were generally in the areas of lower conductivity and perimeter wells. Where nutrient breakthrough was observed, significant declines in total chlorinated VOC concentrations (70-99%) were generally observed. These values correlated well with the results observed from the extraction. For those wells where nutrient arrival was not observed, generally in areas of lower permeability or perimeter wells, only modest contaminant reductions were recorded. Degradation rates of as high as 1-2 ppm per day were observed in the higher concentration areas, greater than 100 ppm, while in areas with lower concentrations, degradation rates of 0.05 to 0.10 ppm per day were observed. There was no evidence of significant degradation product build up in any monitoring well, and many wells with contaminant concentrations below 10 ppm showed contaminant reductions to regulatory allowable levels.

The cost of the pilot system totaled approximately $400,000 with over half the costs associated with sampling and analyses. Most of the sampling and analyses were discretionary and were used to verify the system concept and design. This level of sampling would not be needed during a full-scale bioremediation project. System construction costs were about $90,000 while operating costs were about $30,000 or $0.12 per gallon of water treated. The extensive modeling, hydrogeologic, nutrient transport, and operating cost data developed during this pilot operation suggest that the Northeast Site could be remediated using nutrient injection in approximately 2-3 years at a cost of about $4-6M. From the results of the pilot study, nutrient addition to stimulate existing *in situ* anaerobic biological degradation of chlorinated solvent contaminated soil and ground water appears to be a feasible and cost effective remediation approach at the Pinellas Northeast Site for areas of moderate contaminant levels.

2. SITE INFORMATION

Identifying Information

Facility:	Pinellas Science, Technology, and Research (STAR) Center, formerly the U. S. Department of Energy Pinellas Plant
Location:	Largo, Pinellas County, Florida
OU/SWMU:	Northeast Site
Regulatory Driver:	RCRA
Type of Action:	ITRD Technology Demonstration
Technology:	*In situ* anaerobic bioremediation
Period of operation:	February 1997 to July 1997
Treatment area:	45 ft x 45 ft x 30 ft (60750 ft^3)

Site Background

The Pinellas STAR Center occupies approximately 100 acres in Pinellas County, Florida, which is situated along the west central coastline of Florida (Figure 1). The plant site is centrally located within the county, and is bordered on the north by a light industrial area, to the south and east by arterial roads, and to the west by railroad tracks. The topographic elevation of the Pinellas STAR Center site varies only slightly, ranging from 16 feet MSL in the southeast corner to 20 feet MSL in the western portion of the site. Pinellas County has a subtropical climate with abundant rainfall, particularly during the summer months.

The Northeast Site includes the East Pond and is located in the northeast portion of the Pinellas STAR Center site. The Northeast Site is covered with introduced landscaping grass and contains no permanent buildings. The site contains approximately 6 acres and is generally flat, with slight elevation changes near the pond. Access to the Northeast Site is restricted and protected by fencing.

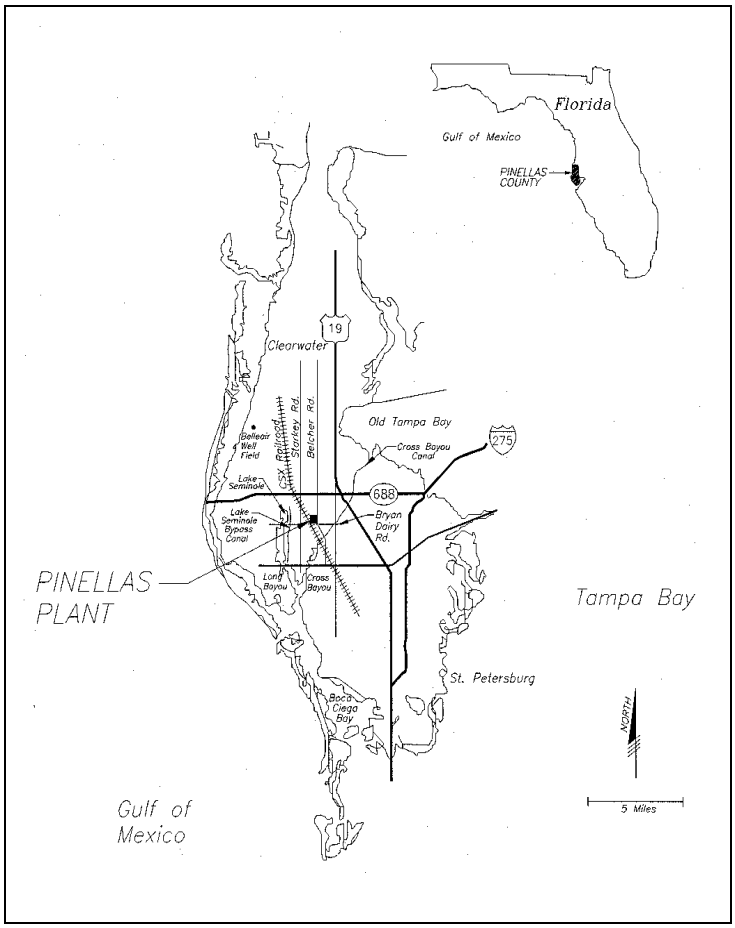


Figure 1. Pinellas STAR Center location.

Site History

The Pinellas Plant operated from 1956 to 1994, manufacturing neutron generators and other electronic and mechanical components for nuclear weapons under contract to the U.S. Department of Energy and its predecessor agencies (SIC Code 9631A-Department of Energy Activities).

The Northeast Site is associated with the location of a former waste solvent staging and storage area. From the late 1950s to the late 1960s, before construction of the East Pond, an existing swampy area at the site was used to dispose of drums of waste and construction debris. The East Pond was excavated in 1968 as a borrow pit. In 1986, an expansion of the East Pond was initiated to create additional storm water retention capacity. Excavation activities ceased when contamination was detected directly west of the East Pond.

The Northeast Site was identified as a Solid Waste Management Unit (SWMU) in a RCRA Facility Assessment (RFA)[1] conducted by EPA Region IV. Subsequently, a RCRA Facility Investigation (RFI)[2] was completed and approved in compliance with the facility's Hazardous and Solid Waste Amendments of 1984 (HSWA) permit.[3]

An Interim Corrective Measures (ICM) Study[4] was developed and submitted to EPA for approval. EPA issued final approval of the ICM in October 1991, and an interim ground water recovery system for the Northeast Site was installed and commenced operation in January 1992. A Corrective Measures Study Report was submitted to EPA in March 1993 and approved in November 1994[5]. A Corrective Measures Implementation Plan was submitted to EPA in March 1996 and approved in June 1996. The current system now consists of seven ground water recovery wells equipped with pneumatic recovery pumps that transfer ground water for temporary storage in a holding tank prior to being pumped to a ground water treatment system.

Release Characteristics

The primary management practice that contributed to contamination at this site was the storage of drums/containers. Because the site was used in the 1950s and 1960s for staging and burial of construction debris and drums, some of which contained solvents, contamination at the Northeast Site is believed to be the result of leakage of solvents or resins from those drums. The Pinellas Northeast Site consists of a shallow ground water aquifer contaminated with a variety of VOCs, including chlorinated solvents such as trichloroethylene, methylene chloride, dichloroethylene, and vinyl chloride. A recent debris removal activity at the site removed multiple buried drums, many of which were empty but contained solvent residue. The ongoing ICM system (pump and treat with air stripping) continues to recover contaminants from the site and has been successful in preventing off-site migration of VOCs.

Site Contacts

Site management is provided by the DOE Pinellas Area Office (DOE/GJO). The DOE/GJO Pinellas STAR Center Environmental Restoration Program Manager is David Ingle [(813)-541-8943]. The technical contact for the Pinellas Plant *in situ* anaerobic bioremediation project is Mike Hightower, the ITRD technical coordinator at Sandia National Laboratories [(505)-844-5499].

3. MATRIX AND CONTAMINANT DESCRIPTION

The anaerobic bioremediation system treated a matrix of soil and ground water to enhance the degradation of chlorinated organic compounds (*in situ*).

Site Geology/Hydrology

Based on analysis of soil borings, details of well construction, and environmental studies at the Pinellas STAR Center, the thickness of the surficial deposit below the site ranges from 25 to 35 feet and is primarily composed of silty sand. Figure 2 shows the primary geologic units at the site. The top of the Hawthorn Group (composed primarily of clay) is encountered at depths approximately 30 feet below ground surface. The thickness of the Hawthorn Group ranges from 60 to 70 feet. The water table at the Northeast Site is generally 3 to 4 feet below the ground surface. The ground water gradient and ground water flow velocity at the site are both very low.

The ground water system at the Pinellas Star Center is composed of three primary units: (1) an upper unit, the surficial aquifer; (2) an intermediate confining unit, the undifferentiated portion of the Hawthorn Group; and (3) a lower unit, the Floridan aquifer. Undifferentiated sediments lie below the surficial aquifer and above the Floridan aquifer in Pinellas County. Because of the low permeability of these sediments in this region, these upper sediments are not considered part of the intermediate aquifer system and are generally considered to be a confining unit in the area of the Pinellas STAR Center.

Measurements performed in the bioremediation study area, including down-hole flowmeter tests, have suggested that the surficial aquifer in the study area is relatively heterogeneous with regard to hydraulic conductivity. These heterogeneities appear in the vertical and horizontal direction. Specifically, zones of reduced (i.e., by a factor of 10 or greater) hydraulic conductivity occur at depths between 10 to 14 feet and 22 to 27 feet. The bulk of the contamination in the bioremediation study area has been detected within these low permeability layers.

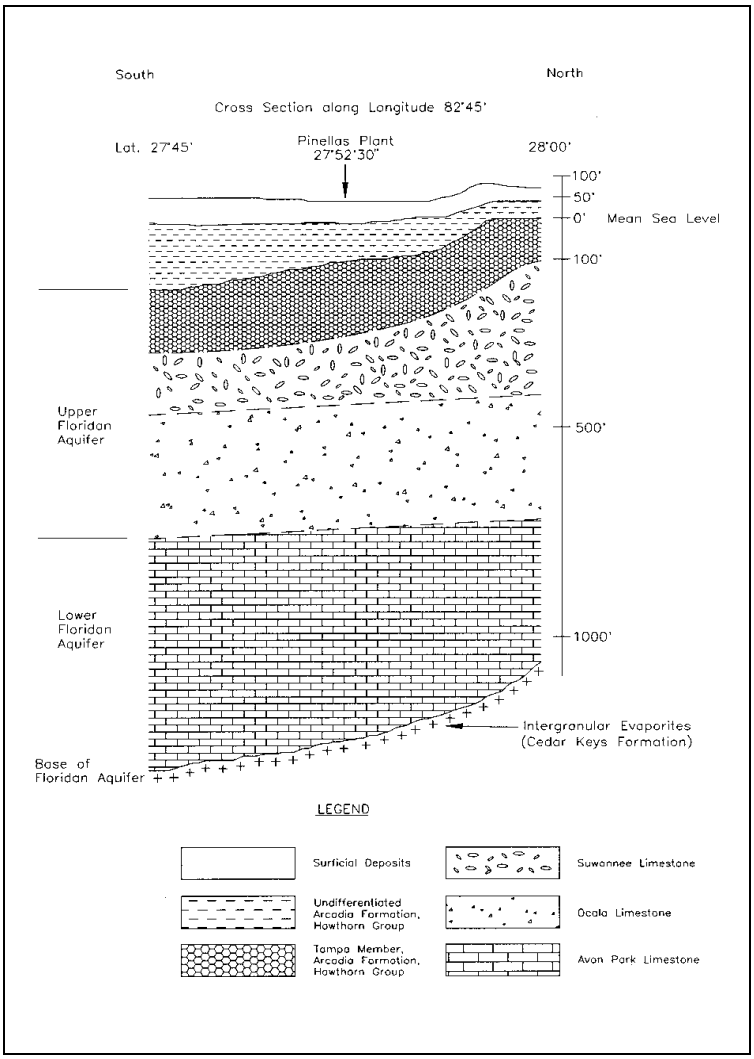


Figure 2. Geologic section at the Pinellas STAR Center.

Nature and Extent of Contamination

The primary contaminant group that the *in situ* bioremediation technology was designed to treat in this application was halogenated VOCs at the Northeast Site in the surficial aquifer. Contaminants of concern (COCs) detected in Northeast Site ground water include 1,1-dichloroethane, 1,1-dichloroethylene, benzene, ethylbenzene, 1,2-dichloroethylene (DCE) (cis and trans isomers), methylene chloride, toluene, trichloroethylene (TCE), tetrachloroethylene, methyl tert-butyl ether, vinyl chloride, xylenes, and chloromethane. The major contaminants of concern at this site, because of their concentrations and cleanup levels are methylene chloride, 1,2-DCE, TCE, toulene, and vinyl chloride. Figure 3 shows a contour map of VOC contamination in ground water at the Northeast Site and in the area selected for the bioremediation pilot-study. The concentrations prior to treatment and the solubilities of primary COCs within selected bioremediation treatment area are summarized in Table 1.

There is some evidence that non-aqueous phase liquid contamination may be present in localized areas at the Northeast Site. VOC concentrations for several COCs exceeded solubility limits in some of the ground water samples taken at the site, and the contaminant release scenario (leakage of solvents or resins from drums stored or buried at the site) is consistent with this type of contamination. While the exact extent and nature of this contaminant phase is unknown, these areas can be a continuing source of ground water contamination unless effectively addressed in a comprehensive site remediation system design.

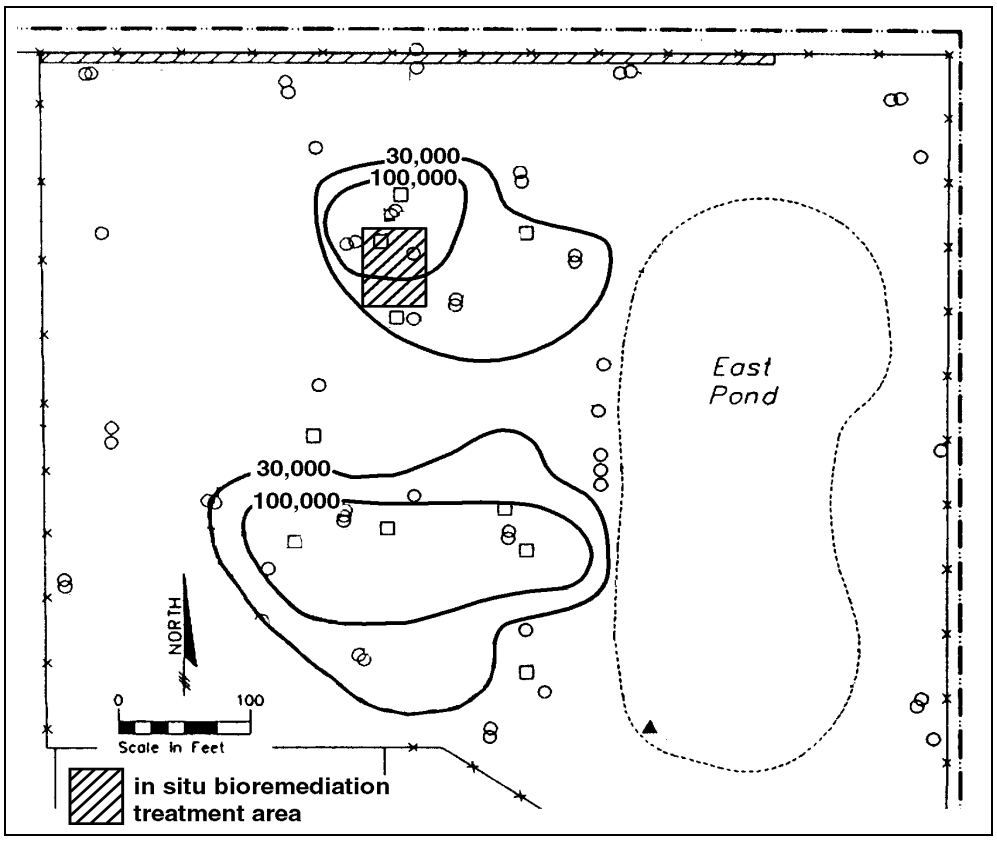


Figure 3. Total VOCs in ground water (in µg/L).

Table 1. Pretreatment concentrations of contaminants.

Contaminant	Ground water		Solubility limit
	Max. conc. (µg/L)	Avg. conc. (µg/L)	(µg/L)@20–25ºC
TCE	1,700,000	46,600	1,100,000
Toluene	2,200,000	45,600	515,000
cis-1,2-DCE	210,000	19,200	800,000
Methylene chloride	760,000	18,450	16,700,000
Vinyl chloride	130,000	9,500	1,10-1,100,000

Matrix Description and Characteristics

The surficial aquifer at this site consists predominantly of saturated beach-type silty sands (see Table 2). A few lenses of more silty materials exist, though no clay lenses occur in the soil being treated. For these soils, the hydraulic conductivities in the horizontal direction range from 10^{-3} to 10^{-5} cm/sec, while the vertical conductivities are approximately 10-100 times lower. The surficial aquifer is highly anaerobic as demonstrated by the dissolved oxygen and Eh values shown in Table 2.

Table 2. Matrix characteristics affecting treatment cost or performance.

Parameter	Value
Soil classification	Silty sand
Clay content	low; 5–10%
Moisture content	mostly saturated (see below)
Hydraulic conductivity $K_{horizontal}$ $K_{vertical}$	$7x10^{-5}$ to $2x10^{-3}$ cm/sec or 0.2–6.6 ft/day; $K_{vertical}$ is approx. 10-100 times less than $K_{horizontal}$, or 0.003 to 0.3 ft/day
Inorganic compounds: Potassium, soluble Nitrate/nitrite Phosphate as P	 2-10 mg/L 0,2-1.0 mg/L 0.1-0.5 mg/:
pH	5.5 to 7.2; mean 7.0
Total organic carbon	4–500 mg/kg; mean 50 mg/kg
Dissolved oxygen	0.1–0.8 mg/L; mean 0.1 mg/L
Eh	–175 to 30 mV; mean –50 mV
Maximum treatment depth: Saturated thickness treated:	approximately 30 ft 25-27 ft

4. TECHNOLOGY DESCRIPTION

This field demonstration evaluated *in situ* anaerobic bioremediation as a technology to treat chlorinated VOCs in soil and ground water. Bacteria metabolize soluble organic and inorganic compounds to provide energy for the growth and maintenance of bacterial cells. The complex organic molecules that bacteria consume are converted to new cells and various simpler compounds, such as carbon dioxide, that are released back into the environment. This process is referred to as biodegradation. Biodegradation has been used very cost effectively for more than a century in public and industrial wastewater treatment systems. Since bacteria occur naturally in both soil and ground water environments, bioremediation technologies attempt to stimulate the activity of these naturally occurring (or introduced bacteria) to degrade contaminants in a cost-effective manner. Bioremediation is being considered more often as the processes that control the biological degradation of contaminants in soil and ground water become better understood.

In Situ Anaerobic Bioremediation Technology Description

In order to produce new bacterial cells, bacteria require carbon, nitrogen, phosphorus, and energy sources, as well as a number of trace minerals. Electrons are released by the biochemical reactions that metabolize complex organic compounds for energy. Biological systems capture this biochemical energy through a series of electron transfer (redox) reactions. The bacteria that are most commonly used in bioremediation systems use organic compounds as their source of carbon and energy; these carbon compounds are referred to as electron donors. Bacterial respiration requires that some chemical compound is available to act as a terminal electron acceptor. Common electron acceptors used by bacteria include oxygen, nitrate, sulfate, Fe^{3+}, and carbon dioxide.

Recently, a class of anaerobic bacteria has been identified that uses halogenated organic compounds as their electron acceptors. The chlorinated VOCs present in the soil and ground water at the Northeast Site are among the halogenated organic compounds that can be used in this manner. Halogenated compounds have a high oxidation state; and when a halogen (e.g., chlorine) is chemically replaced by hydrogen, the oxidation state of the chemical is reduced. This process is referred to as reductive dehalogenation, and it forms the basis of the anaerobic process used by the *in situ* bacteria at the Northeast Site. Under anaerobic conditions, chlorinated compounds can be degraded via reductive dehalogenation reactions to successively lower chlorinated degradation products, and finally to compounds of significantly lower toxicity. This process is illustrated for TCE below.

TCE → DCE → VC → ethylene, ethane
step 1 step 2 step 3

Biological activity is frequently limited by the availability of a single growth factor (e.g. electron acceptor, electron donor, nitrogen, etc.) and supplying the proper growth factor can often stimulate bacterial growth and biodegradation rates. For *in situ* remediation applications, nutrients or electron acceptors are often injected into the contaminated area to enhance the existing microbial degradation processes. Effectively delivering nutrients requires that factors such as site permeability and geochemistry be considered. Each class of contaminant varies in its susceptibility to biodegradation and factors such as aquifer oxidation-reduction potential, microbial ecology, and contaminant toxicity will affect the success of bioremediation at a site. The effective application of in situ bioremediation therefore depends upon careful consideration of the geologic and hydrologic properties at the site and on the type and concentration of contaminants to be treated. Bench scale treatability studies with aquifer soil and ground water samples are highly recommended prior to full-scale implementation of most bioremediation projects.

The application of *in situ* anaerobic bioremediation for the degradation of chlorinated solvents has received significant interest due to the excellent results obtained in laboratory and small pilot-scale applications using these processes. These studies have shown that the injection of simple nutrients can

significantly accelerate the natural degradation of compounds such as PCE, TCE, DCE, carbon tetrachloride, and methylene chloride in soil and ground water. Some companies hold patents on certain aspects of accelerated *in situ* anaerobic bioremediation for the treatment of chlorinated solvents. Sites interested in the use of this technology should be aware that patent related issues might need to be addressed

Evaluations of the monitoring data from the Northeast Site suggested that microbial dechlorination is occurring naturally. DCE and vinyl chloride (VC) are degradation products of TCE that were measured in high concentrations but were not contaminants originally disposed of at the site, which suggests that a population of dechlorinating microorganisms is relatively active at Pinellas. Based on these evaluations and the review of the site hydrologic conditions, it was expected that nutrient injection would be effective in accelerating the anaerobic microbial degradation of the major COCs at the Northeast Site.

Technology Advantages

The treatment of VOC-contaminated soils and ground water using nutrient injection to stimulate and accelerate *in situ* anaerobic bioremediation offers the following advantages:

- contaminants are treated *in situ* with little waste generation,
- contaminant degradation can be relatively fast,
- bioremediation is capable of reducing contaminants to very low levels,
- the process stimulates a microbial population that can continue to feed off the dissolved phase of a continuing source after nutrient injection ceases, and
- often provides a low overall remediation cost relative to other technologies.

Technology Limitations

The treatment of VOC-contaminated soils and ground water using nutrient injection to stimulate and accelerate i*n situ* anaerobic bioremediation offers the following limitations:

- contaminant degradation enhancement is dependent on adequate nutrient delivery to all areas of contamination before the nutrients are directly metabolized, which often is primarily a function of site hydrogeology and the appropriate mixing of nutrients, contaminants, and active microbes,
- site conditions (e.g., soil and ground water chemistry, reductive processes, etc.) must be conducive to the stimulation of biological activity to be effective,
- bioremediation will not directly degrade contaminants occurring in an immiscible phase,
- high concentrations of contaminants often are toxic to microorganisms,
- bioremediation may be difficult to optimize at sites with multiple contaminants of concern,
- incomplete biodegradation of contaminants can lead to the generation of degradation products that are just as toxic or even more so than the parent contaminants, and
- regulatory concerns over chemical injections into aquifers.

Treatability Study

Through the ITRD Program, laboratory batch and column biotreatment studies were performed under anaerobic conditions using aquifer sediments and ground water from the Northeast Site. These studies were used to assess methods for stimulating and/or optimizing the existing anaerobic biological activity at the Northeast Site.[6] The laboratory studies generated information on contaminant degradation rates, the reductive dechlorination process, and byproduct formation for several different nutrient combinations and concentrations. The nutrient mixtures used included combinations of trace nutrients such as potassium and phosphorus, and other nutrients such as sodium benzoate, sodium lactate, methanol, and casamino acids. Nutrient concentrations generally ranged from 100-400 ppm.

The study showed that two nutrient combinations, both of which included methanol, were effective in reducing both TCE and methylene chloride and that degradation rates of as high as 1-2 ppm/per day were achievable for TCE. The results also showed that with these nutrient mixtures dehalogenation of TCE did not stop at any intermediate degradation products. In the case of toluene and trace contaminants, it was not determined from this laboratory study what conditions would optimize their utilization or degradation. Under the existing site conditions, toluene can degrade through fermentation, while simple electron acceptors are available to accelerate toluene treatment.

Based on the laboratory data, a preliminary full-scale bioremediation system cost and performance estimate was developed. From these engineering estimates, in situ anaerobic bioremediation appeared to be a very cost effective and rapid technique for treating ground water of low to moderate contaminant concentration (less than 200 ppm) at the Northeast Site. It was expected that areas of significantly higher contaminant concentration would probably need to be treated by a more aggressive treatment method.

Pinellas In-Situ Bioremediation System Description

Based on the laboratory treatability study results, and the engineering cost and performance estimates of in situ anaerobic bioremediation, a large pilot-scale remediation system was designed and constructed at the Northeast Site. The system was operated for approximately five months to assess the field performance of this technology and to identify the optimum operating parameters for a full-scale system. Historical data was used to select an area within the Pinellas Northeast Site that was understood to contain the entire suite of chlorinated compounds found at the site and with contaminant levels ranging from at least 100-200 ppm. If the initial concentrations were too high, there was a potential that the microbial population would be inactive. If the initial concentrations were too low, contaminant degradation could be difficult to monitor. Thus, an area expected to have mid-range contamination levels, as shown in Figure 3, was chosen for the *in situ* bioremediation pilot-study.

The hydraulic modeling, design, construction, and operation of the bioremediation pilot system and the associated monitoring well network are discussed in detail in this section. The operational concept developed for the pilot system was to create a closed-loop ground water recirculation system where ground water could be continually circulated through the treatment area while nutrients were added to the circulated water to accelerate in situ contaminant degradation. This was expected to minimize external ground water influence on performance assessment results, minimize nutrient loss and accelerate biodegradation, and eliminate the need for ground water treatment or disposal. A large number of clustered monitoring wells were also installed in the treatment area in order to assess contaminant degradation and system performance throughout all levels of the treatment area.

Figure 4 shows the general layout of the treatment area and perimeter and cluster monitoring wells . Four fully-screened monitoring wells were installed in the perimeter of the study area to perform flowmeter testing of the aquifer matrix. The flowmeter testing determined the relative hydraulic conductivities of the zones indicated in the cross section in Figure 5. The central area is approximately 45 ft x 45 ft.

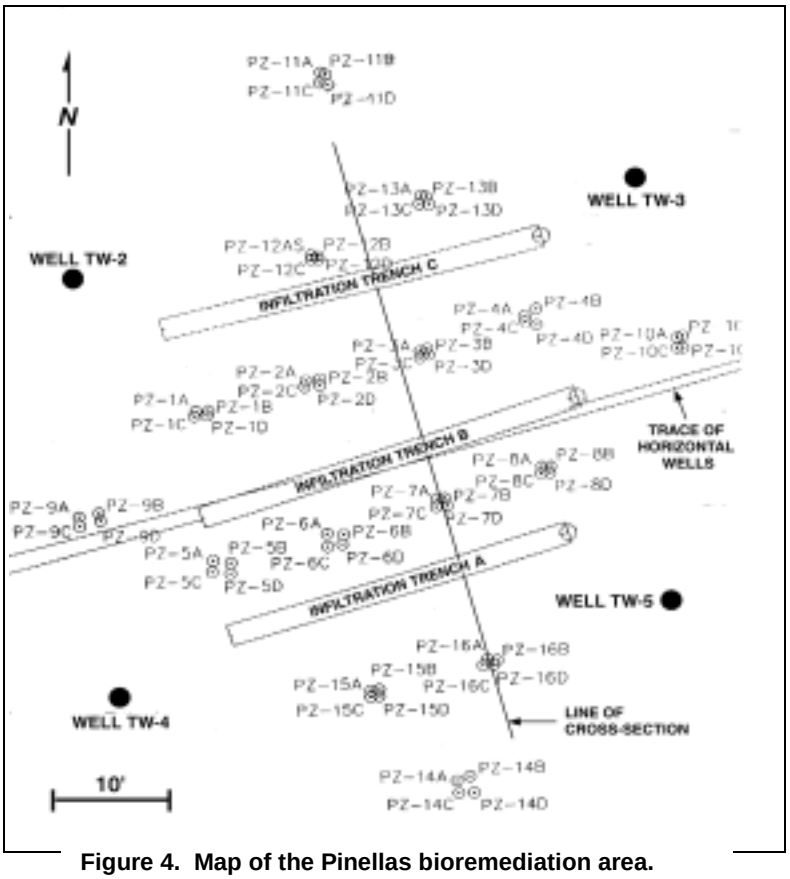


Figure 4. Map of the Pinellas bioremediation area.

The overall design, configuration, and location of the extraction and injection wells were developed based on a number of system performance assessments using MODFLO, a two-dimensional ground water flow model. The modeling looked at nutrient delivery and movement through the treatment area based on several possible vertical and horizontal system configurations and well locations and the site hydrogeologic data. This modeling effort suggested that ground water circulation using horizontal wells and trenches would provide better nutrient delivery across the horizontal layers of relatively low vertical hydraulic conductivity where contaminant concentrations were highest.

To achieve a vertical hydraulic gradient, a horizontal extraction well with a 30 foot screened section was installed through the center of the treatment area in a zone of higher conductivity 16 ft below ground surface (bgs). The ground water extracted from the horizontal well was then returned to the aquifer via one of the four infiltration points shown in Figure 5. The first three points were gravel-filled, surface trenches (A, B, & C) which were 30 ft long, 8 ft deep, and at least 2 ft wide. The fourth infiltration point (D) was a horizontal well similar to the extraction well but installed at 26 ft bgs. MODFLOW simulations indicated that this well and trench system would create a general flow pattern through the treatment area as shown in Figure 6, under nominal operating conditions. The system was designed to allow reversal of the extraction and infiltration points, providing flexibility in optimizing nutrient delivery to the different aquifer levels across the treatment area if needed.

The ground water monitoring system shown in Figure 6 included 16 clusters of 4 sampling points to create a three-dimensional monitoring network of the treatment area. These monitoring points were installed at discrete depths starting at the depth corresponding to the elevation of the bottom of the trenches. The “A” depth was 8-10 ft bgs, the “B” depth was 12-14 ft bgs, the “C” depth was 18-20 ft bgs, and the “D” depth was 22-24 ft bgs. The “B” and “D” depths were chosen to correspond with the layers of lower hydraulic conductivity within the study area, which contained the maximum contaminant concentration. This was an effort to monitor system performance in actual worst case conditions.

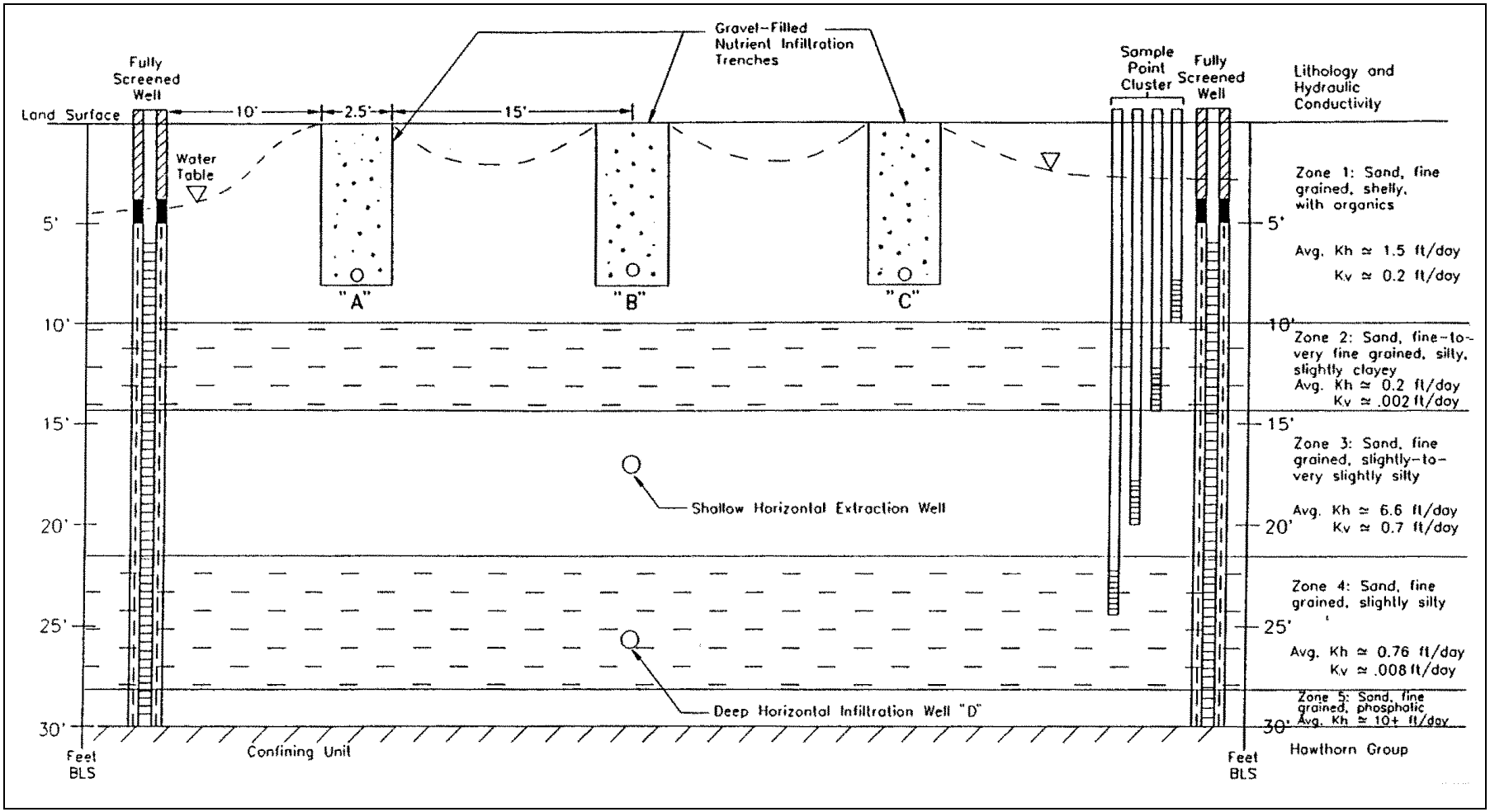


Figure 5. Cross section of treatment area looking west.

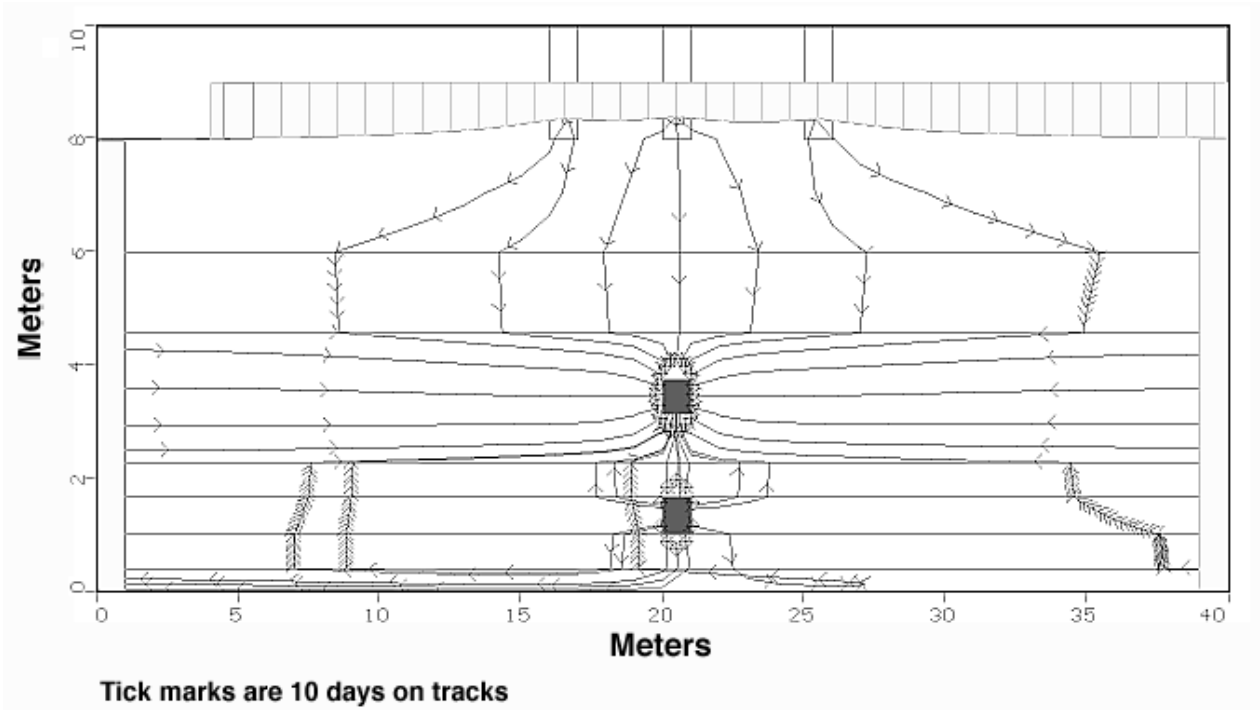


Figure 6. MODFLO model of system ground water flow patterns and transit times.

Treatment System Schematic and Operation

Figure 7 is the process schematic for operation of the pilot anaerobic biotreatment system. In this system, the extracted ground water was pumped from the horizontal extraction well, monitored continuously for contaminant concentrations with an automatic field GC, had nutrients added in-line, and was then returned to the aquifer through the infiltration trenches and the horizontal infiltration well. The trenches had float switches installed just below ground surface that operated solenoid valves allowing ground water and nutrients to enter at a steady rate without overflow. When all three surface trenches were filled to their recharge capacity, a fourth solenoid valve would open to allow the nutrient rich ground water to enter the aquifer from the lower horizontal infiltration well in the treatment area.

Each infiltration point was separately metered for flow, and each infiltration point had a separate stock tank of nutrient solution so that the amount introduced into each point could be calibrated against the corresponding ground water flow. Total ground water flow through each infiltration point and the nutrient solution used from each stock tank were recorded daily. The use of individual stock tanks also provided the capability to conduct a multi-tracer study. The tracers were introduced into the nutrient solution tanks in a controlled, continuous release so that nutrient transport could be easily monitored. Because both upward and downward ground water movements were being studied, two different tracers were used. Bromide was selected for tracking the upward flow from the horizontal infiltration well and iodide was used for tracking the downward flow from the surface trenches.

An enclosed equipment control pad was located approximately 50 feet east of the system. All nutrient drums, nutrient pumps, flow meters, solenoid valves, and a filter were located at the control pad.

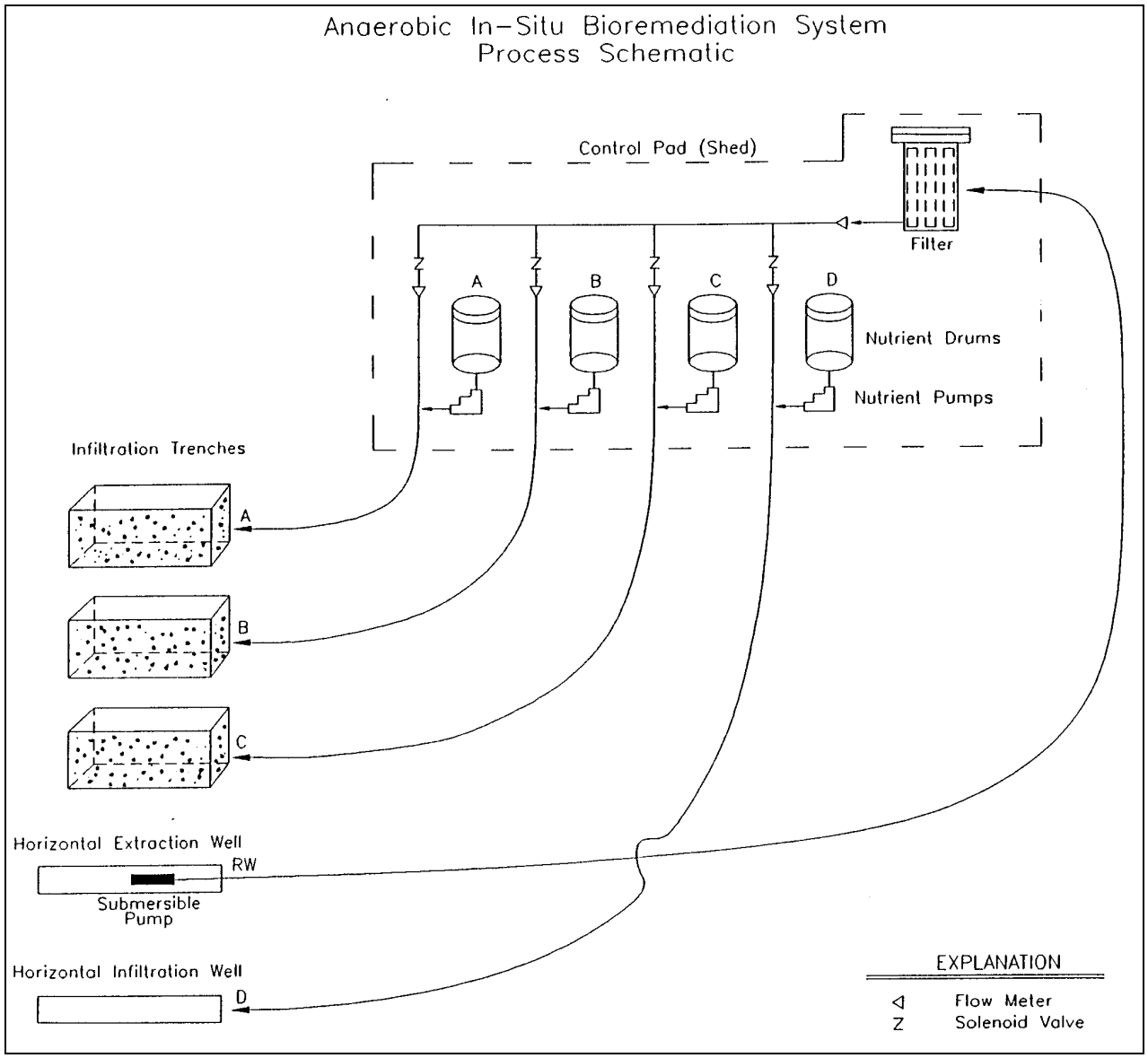


Figure 7. Bioremediation pilot system process schematic diagram.

Key Design Criteria

The *in situ* anaerobic bioremediation pilot system was designed for two main objectives:

- develop a nutrient delivery system capable of providing a mixture of nutrients to the subsurface within the heterogeneous aquifer, such that the nutrients will be delivered to all levels in the treatment area within an approximately 6-month operating period, and
- create a closed-loop ground water recirculation system that would minimize external influences and losses and requires no ground water disposal.

Operating Parameters

Operating parameters were adjusted slightly during the pilot test to help optimize operating conditions for the bioremediation system. The major operating parameters needed to assess the performance and cost of the bioremediation system were considered to be pumping rates, nutrient concentrations, tracer concentrations, and well redevelopment frequency. The general operating parameters for the system are summarized in Table 3.

Table 3. Operating parameters affecting treatment cost or performance.

Parameter	Value or Specification
Optimal pumping rate from horizontal extraction well	1.5 gpm
Optimal pumping rate to infiltration trenches A, B, and C	0.2 gpm each
Optimal pumping rate to horizontal infiltration well (D)	0.9 gpm
Concentration of methanol added to the ground water	60 ppm
Concentration of sodium benzoate added to the ground water	120 ppm
Concentration of sodium lactate added to the ground water	180 ppm
Concentration of iodide to trenches A, B, and C	250 ppm
Concentration of bromide to horizontal infiltration well (D)	250 ppm
Frequency of redevelopment of horizontal extraction well	average of once every 3 weeks
Frequency of redevelopment of horizontal infiltration well	once

The horizontal extraction well is located at a depth of 16 feet bgs in a zone of relatively high hydraulic conductivity. A pumping rate of 1.5 gpm was sustainable through this well. The horizontal infiltration well was at a depth of 26 feet bgs in a zone of somewhat lower hydraulic conductivity, however, it could accept a pumping rate of 0.9 gpm of the recirculated ground water under a pressure gradient of 5-10 psi above the ambient hydraulic head. The infiltration trenches are 8 feet deep and located in a zone of lower hydraulic conductivity. Each trench accepted only approximately 0.2 gpm of recirculated ground water.

Nutrient concentrations added to the ground water were based on the results of the original ITRD treatment study and follow-on discussions by the ITRD committee.[6] Methanol, benzoate, and sodium lactate, at concentrations of 60, 120, and 180 ppm, respectively, were added. This mixture of electron donors was used to provide nutrients that would be used at different rates by the bacteria in the aquifer to degrade the major COCs so that the reducing power could be delivered to all treatment levels. Methanol and benzoate additions were initiated on February 12, 1997 and discontinued on June 30, 1997. Lactate was added from February 27, 1997 to June 23, 1997. The tracer concentrations added were used to insure that the breakthrough of nutrient rich ground water could be detected at the monitoring point locations. Iodide, at a concentration of 250 ppm, was added to trenches A, B, and C. Bromide, at a concentration of 250 ppm, was added to the horizontal infiltration well (D). All tracer additions were initiated on March 7, 1997. Tracer additions to trenches A, B, C, and well D were discontinued on June 4, May 13, May 28, and April 25, respectively.

Due to subsurface conditions at the Northeast Site and possible fouling of well screens, redevelopment of the horizontal wells by hydraulic surging was needed to ensure efficient operation of the system. The horizontal extraction well was redeveloped on February 24, March 6, March 13, March 31, April 8, April 22, June 4, and June 16. The horizontal infiltration well was redeveloped only once on June 3, 1997.

5. *IN SITU* ANAEROBIC BIOREMEDIATION SYSTEM PERFORMANCE

The bioremediation pilot operations at the Northeast Site were conducted to assess the applicability of nutrient injection to accelerate the degradation of the chlorinated contaminants of concern and to identify optimal operating parameters. These data were used to determine the expected costs and performance of a full-scale system at the site.

Demonstration Objectives and Approach

The objectives of the pilot *in situ* anaerobic bioremediation project were as follows:

1. Convert chlorinated VOCs in the ground water at the Northeast Site to innocuous biodegradation products using *in situ* anaerobic biodegradation,
2. Determine the suitability and effectiveness of this technology on site soils and ground water, and estimate the time period needed to meet cleanup objectives,
3. Evaluate the horizontal extraction well and infiltration gallery design configuration for full-scale implementation and determine hydraulic parameters, such as flow rates, residence times, flowpaths, and treatment levels,
4. Determine optimal operating parameters and conditions for treatment and potential scale-up, such as nutrient concentrations, nutrient half-lives, and contaminant degradation rates,
5. Collect sufficient cost data to support cost estimates for a potential full-scale system; and
6. Conduct the pilot test in a location that is representative of site-wide conditions, is not impacted by neighboring treatment operations (rotary steam stripping) and does not detrimentally impact ongoing ground water recovery systems.

Performance Evaluation Criteria

The performance criteria considered in evaluating this *in situ* anaerobic bioremediation system included:

- nutrient transport and utilization in the remediation study area,
- contaminant degradation rates and the reduction in mass of the contaminants,
- fate of chlorinated solvent degradation compounds, and
- levels to which contaminants can be reduced.

The evaluation data were collected by a monitoring program that included: semimonthly sampling for VOCs, methane, ethane, and ethylene; weekly tracer sampling; semimonthly sampling of nutrients following tracer breakthrough; weekly measurements of water levels until ground water flow conditions stabilized; and maintenance of a daily log to record operational data.

Performance Summary

Table 4 summarizes the pretreatment (February 1997) and post-treatment (July 1997) contaminant concentrations at each of the 64 monitoring points within the bioremediation treatment area, as well as the period of time required for the nutrients to reach each monitoring point. The conceptual model of this microbially mediated, *in situ,* reductive dechlorination system requires that nutrients (primarily electron donors), contaminants, and adapted microorganisms reside or mix at the appropriate ratios and concentrations for significant contaminant reduction to occur.

Table 4. Pretreatment and post-treatment contaminant concentration at the Pinellas Plant in situ bioremediation treatment area.

Well #	Time to nutrient breakthrough in weeks	Toluene			Methylene Chloride			TCE			cis-1,2-DCE			Vinyl chloride			Total chlorinated VOCs		
		before	after	decline %	before	after	decline %	before	after	decline %	before	after	decline %	before	after	decline %	before	after	decline %
1A	10	47	58	-23	ND	<5.0	-	ND	<1.0	-	ND	<1.0	-	ND	<1.0	-	18	37	-104
1B	12	ND	13	-	ND	<5.0	-	ND	<1.0	-	220	<1.0	99	880	16	98	1,100	37	97
1C	-	ND	<1.0	-	ND	<5.0	-	ND	<1.0	-	ND	<1.0	-	22	54	-145	22	56	-156
1D	4	310	310	0	ND	<25	-	ND	<5.0	-	630	<5.0	99	640	<5.0	99	1,270	195	85
2A	11	1,600	130	92	ND	<10	-	ND	<2.0	-	ND	<2.0	-	83	<2.0	98	113	13	89
2B	10	100	700	-600	ND	<50	-	ND	<10	-	ND	<10	-	16	<10	38	27	15	44
2C	12	210	<10	96	ND	<50	-	ND	110	-	ND	450	-	12	990	-8150	12	1,550	-12817
2D	4	2,200	400	82	1,400	<50	96	420	<10	98	4,200	<10	99	3,500	<10	99	9,520	0	99
3A	14	190	1100	-479	ND	<250	-	ND	<50	-	31	<50	-	240	<50	80	291	0	99
3B	-	1,900	12000	-532	ND	<1200	-	ND	370	-	1,900	21000	-1005	11,000	14000	-27	12,900	35,370	-174
3C	14	9,800	7500	23	1,500	<1000	33	280	<200	29	6,600	1500	77	11,000	4100	63	19,380	5,600	71
3D	5	1,900	1500	21	3,800	<250	93	560	<50	91	1,900	<50	97	2,700	150	94	8,960	204	98
4A	10	3,600	3500	3	ND	<1200	-	ND	<250	-	260	<250	-	490	<250	50	750	0	99
4B	10	190,000	74000	61	25,000	<25000	-	210,000	20000	90	96,000	110000	-15	37,000	12000	68	368,000	142,000	61
4C	-	4,800	20000	-317	ND	<5000	-	ND	<1000	-	4,200	2500	40	12,000	6500	46	16,200	9,000	44
4D	7	7,800	16000	-105	ND	<2000	-	ND	<400	-	ND	4700	-	ND	3700	-	0	8,400	-
5A	10	470	62	87	ND	<25	-	ND	<5.0	-	ND	<5.0	-	ND	<5.0	-	0	9	-
5B	-	1,400	3000	-114	ND	<500	-	1,400	730	48	860	1700	-98	1,500	260	83	3,890	2,690	31
5C	10	130	590	-354	ND	<250	-	ND	<50	-	9	67	-644	58	57	2	117	124	-6
5D	5	1,500	1700	-13	3,300	<120	96	560	<25	96	1,600	140	91	1,800	68	96	7,260	208	97
6A	10	17	15	12	ND	<5.0	-	ND	<1.0	-	ND	<1.0	-	ND	14	-	0	18	-
6B	12	440	2500	-468	ND	<120	-	440	320	27	25	430	-1620	52	55	-6	517	805	-56
6C	12	530	1400	-164	680	<1000	-	230	<200	13	800	16000	-1900	840	14000	-1567	2,580	30,000	-1063
6D	4	2,800	980	65	ND	<120	-	ND	<25	-	4,600	48	99	3,400	31	99	8,000	79	99
7A	6	2,000	160	92	49	<10	80	ND	<2.0	-	14	4	71	67	50	25	152	69	55
7B	7	250	2100	-740	ND	<120	-	600	200	67	ND	1200	-	150	1400	-833	750	2,800	-273
7C	10	100	1300	-1200	ND	<100	-	ND	<20	-	31	250	-706	94	280	-198	125	530	-324
7D	4	1,600	1600	0	ND	<120	-	ND	<25	-	3,600	59	98	4,600	43	99	8,200	102	99
8A	6	2,300	4000	-74	810	<500	38	ND	1900	-	350	3400	-871	700	1300	-86	1,860	6,600	-255
8B	-	71,000	100000	-41	190,000	190000	0	160,000	240000	-50	210,000	170000	19	38,000	20000	47	598,000	620,000	-4
8C	8	150	840	-460	140	<100	29	ND	<20	-	120	59	51	320	63	80	580	122	79
8D	4	2,400	940	61	2,900	<100	97	370	<20	95	3,800	68	98	4,500	43	99	11,570	111	99

Table 4. Pretreatment and post-treatment contaminant concentration at the Pinellas Plant in situ bioremediation treatment area.

Well #	Time to nutrient breakthrough in weeks	Toluene			Methylene Chloride			TCE			cis-1,2-DCE			Vinyl chloride			Total chlorinated VOCs		
		before	after	decline %	before	after	decline %	before	after	decline %	before	after	decline %	before	after	decline %	before	after	decline %
9A	15	46	980	-2030	ND	<100	-	ND	<20	-	ND	<20	-	990	25	97	990	49	95
9B	12	ND	<2500	-	160,000	140000	13	31,000	<2500	92	80,000	21000	74	18,000	21000	-17	289,000	182,000	37
9C	-	ND	97	-	ND	<120	-	ND	96	-	ND	1200	-	ND	1200	-	0	2,496	-
9D	8	ND	<500	-	ND	<2500	-	ND	<500	-	56,000	21000	63	9,000	34000	-278	65,000	55,000	15
10A	10	9,900	2400	76	ND	<250	-	ND	<50	-	ND	77	-	ND	190	-	0	342	-
10B	10	2,200,000	110000	95	760,000	240000	68	1,700,000	74000	96	170,000	64000	62	130,000	25000	81	2,950,000	403,000	86
10C	14	1,000	1200	-20	ND	<250	-	ND	370	-	21,000	520	98	7,000	54	99	28,057	997	96
10D	6	19,000	850	96	2,400	<100	96	1,200	<20	98	21,000	100	99	21,000	160	99	45,600	260	99
11A	-	8	350	-4275	ND	<50	-	ND	<10	-	5	<10	-	21	<10	52	34	18	47
11B	-	71	4200	-5815	86	1600	-1760	380	130	66	170	680	-300	400	560	-40	1,036	3,026	-192
11C	-	ND	320	-	ND	<50	-	ND	16	-	ND	160	-	ND	240	-	0	416	-
11D	-	30	530	-1667	ND	<100	-	ND	22	-	390	960	-146	900	1400	-56	1,290	2,382	-85
12A	8	230	930	-304	ND	<120	-	ND	<25	-	ND	<25	-	19	<25	-	32	0	99
12B	-	56	250	-346	22	470	-2036	170	42	75	79	220	-178	310	170	45	602	917	-52
12C	-	ND	92	-	ND	<100	-	ND	<20	-	ND	260	-	ND	1100	-	0	1,360	-
12D	7	72	760	-956	7	<50	-	ND	<10	-	78	190	-144	180	290	-61	277	492	-78
13A	-	7,500	140	98	ND	<25	-	ND	<5.0	-	ND	<5.0	-	ND	<5.0	-	0	60	-
13B	-	68,000	47000	31	ND	<5000	-	ND	<1000	-	33,000	8100	75	36,000	24000	33	69,000	32,100	53
13C	-	ND	<50	-	ND	<250	-	ND	4000	-	ND	2800	-	ND	770	-	0	7,570	-
13D	6	47	1200	-2453	ND	<100	-	ND	<20	-	31	190	-513	100	300	-200	142	490	-245
14A	11	ND	<1000	-	ND	<5000	-	82,000	6000	93	65,000	56000	14	19,000	45000	-137	166,000	107,000	36
14B	-	ND	5800	-	ND	<25000	-	380,000	300000	21	ND	390000	-	95,000	56000	41	475,000	746,000	-57
14C	-	ND	19	-	ND	<50	-	ND	210	-	ND	280	-	ND	150	-	0	640	-
14D	6	ND	1600	-	ND	<1000	-	97,000	530	99	18,000	7800	57	ND	7200	-	115,000	15,530	86
15A	8	26	120	-362	ND	<25	-	440	70	84	110	230	-109	55	160	-191	605	473	22
15B	12	690	1800	-161	ND	<1000	-	2,000	14000	-600	570	12000	-2005	170	1600	-841	2,740	27,600	-907
15C	-	ND	76	-	ND	<25	-	ND	110	-	ND	270	-	ND	280	-	0	660	-
15D	5	1,300	1100	15	1,100	<100	91	1,600	43	97	2,500	410	84	4,500	440	90	9,700	893	91
16A	12	120,000	47000	61	ND	<5000	-	6,000	<1000	83	110,000	13000	88	27,000	35000	-30	143,000	48,000	66
16B	17	39,000	7900	80	ND	<1000	-	ND	6000	-	51,000	3300	94	50,000	4100	92	101,000	13,400	87
16C	-	140,000	48000	66	28,000	<5000	82	310,000	24000	92	240,000	88000	63	48,000	9500	80	626,000	121,500	81
16D	6	1,000	1700	-70	ND	<250	-	ND	<50	-	21,000	210	99	7,000	1400	80	28,000	1,610	94

Due to the nature of the subsurface hydrogeology, transport and mixing times for the added nutrients will vary across the site, and depending on system design and operation, nutrient delivery to some portions of the aquifer could require significant amounts of time. Therefore, good system performance often requires nutrients that will not be consumed immediately at an injection location and can be transported quickly and efficiently through the subsurface to all levels of the treatment areas.

System Hydraulics and Nutrient Fate and Transport

At the pumping rate of 1.5 gpm, approximately 250,000 gallons of water, or about two pore volumes, were recirculated through the pilot study treatment area over a five-month period. Tracers were used to identify nutrient breakthrough at each monitoring point for the first ten to twelve weeks of system operations. When over 50% of the monitoring points showed breakthrough, tracer additions were stopped and nutrient concentrations were monitored directly. Tracer and nutrient breakthrough were defined as a concentration greater than 10% of the injected concentrations. Tracer breakthrough was observed earliest (1-2 weeks) in several of the "D"-level wells in the central part of the treatment area. The "B" and "C" level wells showed much slower tracer and nutrient breakthrough and the perimeter wells (Wells 9, 10, 11, and 14) showed limited breakthrough during operations. Of the 48 central monitoring points, 43 wells (90%), experienced breakthrough during the first 16 weeks of operation. Of the wells showing breakthrough in the central treatment area, 77% did so in the first two to three months of system operation. Overall, Levels A, B, C, and D had 88%, 81%, 81%, and 100% respectively, of their monitoring points during the first 16 weeks of operation. These results suggest that though some of the recirculated water may have escaped from the treatment area in levels A and D, water was effectively circulated within the central treatment area of the pilot system.

The tracer and nutrient breakthrough observations were consistent with model predictions. Based on initial modeling with a flow rate of 2 gpm, it was expected that nutrient delivery to the "B" level could take three to four months. It was hoped that this flow rate could be achieved from the extraction well, though a flow of only 1.5 gpm was sustained. A higher flow rate might have improved nutrient delivery to the "B" level monitoring points. From field observations, it appears that the extraction well efficiency was reduced in part due to borehole skin effects caused by the drilling fluid used during installation. BioboreTM by Baroid was used by the drilling contractor and appears not to have degraded as well as expected. Additionally, the infiltration trenches accepted a smaller volume of water than was initially expected, which in turn limited nutrient delivery into the "A" and "B" level monitoring points.

Since enhanced bioremediation depends on adequate nutrient delivery, bioremediation at this site will be controlled by the rate at which nutrients can be delivered into the middle and identified lower permeability zones. This is one reason why the two horizontal well system was implemented, since it allows for reversing the injection and extraction wells and providing more flexibility in delivering nutrients to all levels in the aquifer. However, in order to minimize complications in evaluating the operational performance of the pilot system, reversing the operation of the two horizontal wells was not exercised during the pilot operations. Based on the results of this pilot study, it appears that a properly designed and operated system can deliver nutrients to all of the aquifer at this site within six to eight months.

Nutrient Fate Assessment

For this pilot study, a mixture of electron donors was selected based on the consideration that the relative degradation rates for the different compounds would allow for the delivery of the reducing power of the nutrients to be spread throughout the treatment system. Lactate was used because it is a readily available carbon source that should be quickly oxidized to acetate, which is expected to degrade much slower. Benzoate was expected to degrade slower than lactate but would also yield partial oxidation products such as acetate that again should take longer to degrade. Methanol was expected to degrade slower than lactate, but faster that benzoate, while also acting as an electron donor to accelerate biodegradation of methylene chloride.

During system operations, sodium benzoate was detected in 59 monitoring points. Of these, 5 had reported concentrations higher than the initial feed concentrations and were not included in the calculations. Using the remaining 54 data points, the average half-life of the nutrients in the aquifer were calculated to be about 110 days, with the calculated half-lives ranging from 12 to 949 days. The 110-day nutrient half-life should be considered a minimum in that dilution, dispersion, and retardation effects were not accounted for due to the difficulty in assessing their relative contributions to the observed concentration decreases.

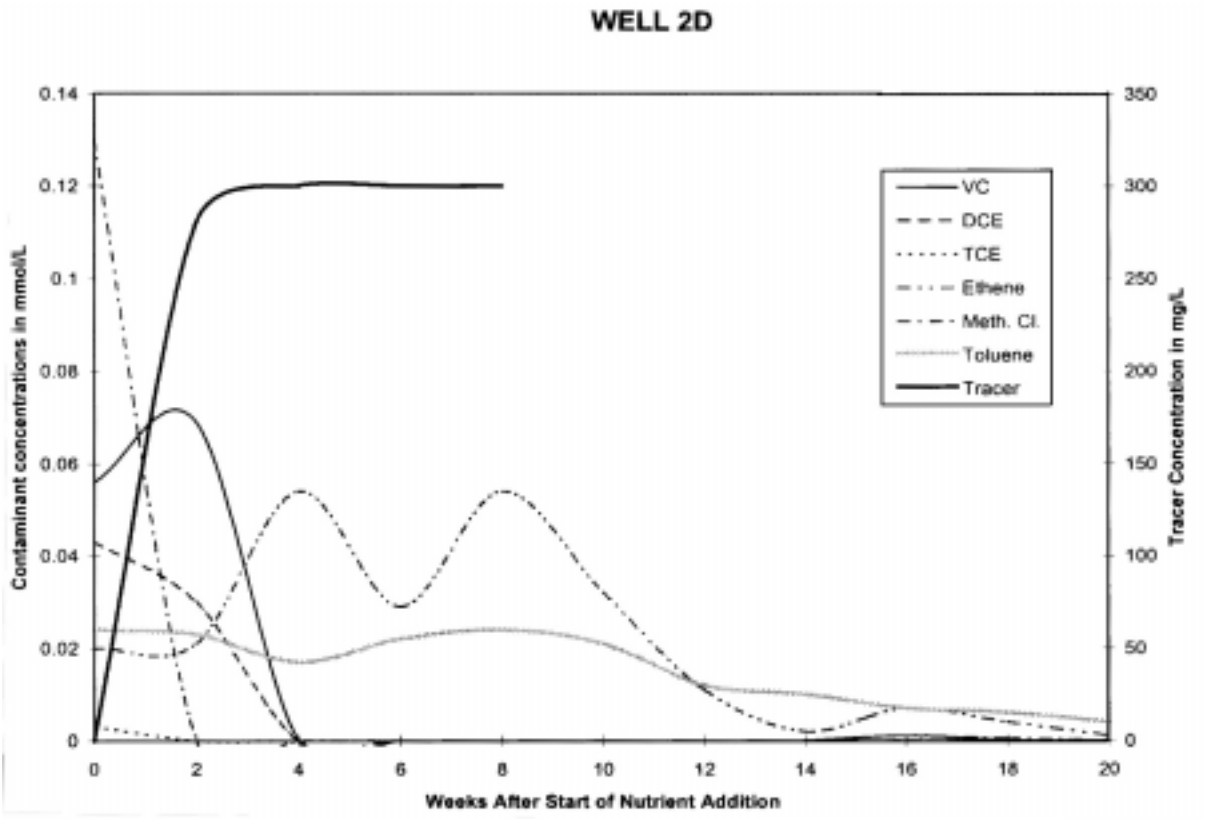
Similar calculations for lactate proved even more difficult due to the inability to resolve lactate/acetate contributions in the analytic methods used. It should be noted, however, that the observed concentrations at several locations in the pilot study area yielded lactate/acetate concentrations near or even above the initial lactate injection concentration of 180 mg/l. This suggests that lactate/acetate half lives in this system of a year or more are possible or that benzoate was being metabolized to acetate. The methanol concentrations varied widely across the treatment area. At some points, methanol concentrations in excess of ten times the added concentration were reported. This suggests that components in the ground water may have interfered with the laboratory analysis.

Together, these results suggest that the nutrients necessary to enhance bioremediation at this site were successfully delivered to areas reached by the injected water. The detection of significant concentrations of benzoate, methanol, and lactate/acetate throughout the treatment at the end of the pilot system operation suggests that the bioavailable reducing power from the injected nutrients were not a limiting factor for this pilot effort and should not be a limiting factor in the operation of a properly designed full-scale system. Based on the system operation, nutrient delivery can be expected to occur in all areas of the aquifer including the middle and lower permeability areas within the effective half-lives (four months to a year) determined for these nutrients.

Contaminant Degradation and Reduction Rates

Contaminant levels encountered at the different monitoring points within the treatment area generally ranged from 10 to 400 ppm total chlorinated VOCs, with one monitoring point location in Level “B” had a concentration of about 2900 ppm. The bioremediation system at this site was designed to develop a recirculation cell within the aquifer creating complex, three-dimensional, ground water and contaminant mixing, making the evaluation of system performance more complicated. Because of the mixing and recirculation of the ground water, temporal variations in contaminant levels in individual monitoring points could be expected. Therefore, it was important to look at contaminant reductions across the whole site, at various treatment levels, at individual wells, and in the extraction well to help assess system performance and define actual contaminant reductions due to biological treatment.

As shown in Table 4, in the wells where nutrient breakthrough, chlorinated VOC concentrations were commonly observed to fall by 60%–99% from their pretreatment levels in as little as four to eight weeks after nutrient arrival. In wells with at least six weeks of nutrient availability, TCE was reduced by 94%, DCE by 54%, vinyl chloride by 58%, methylene chloride by 60%, and toluene by 80%. In wells where nutrient breakthrough was not evident or of short duration, there was a reduction of only 10-15$ in total chlorinated VOCs and toluene. These results suggest that though contaminant reduction in part is probably the result of ground water mixing and contaminant redistribution, contaminant reduction is significantly greater in wells where nutrients are available. Likewise, because of the ground water recirculation, increases in contaminant levels in some wells should be expected. Contaminant increases were observed primarily in wells with lower (~1 ppm) concentrations. Many of the increases observed were for DCE or VCE, which is consistent with the reductive dechlorination process. Significantly fewer concentration increases were observed for TCE and methylene chloride in the wells with long term nutrient availability.



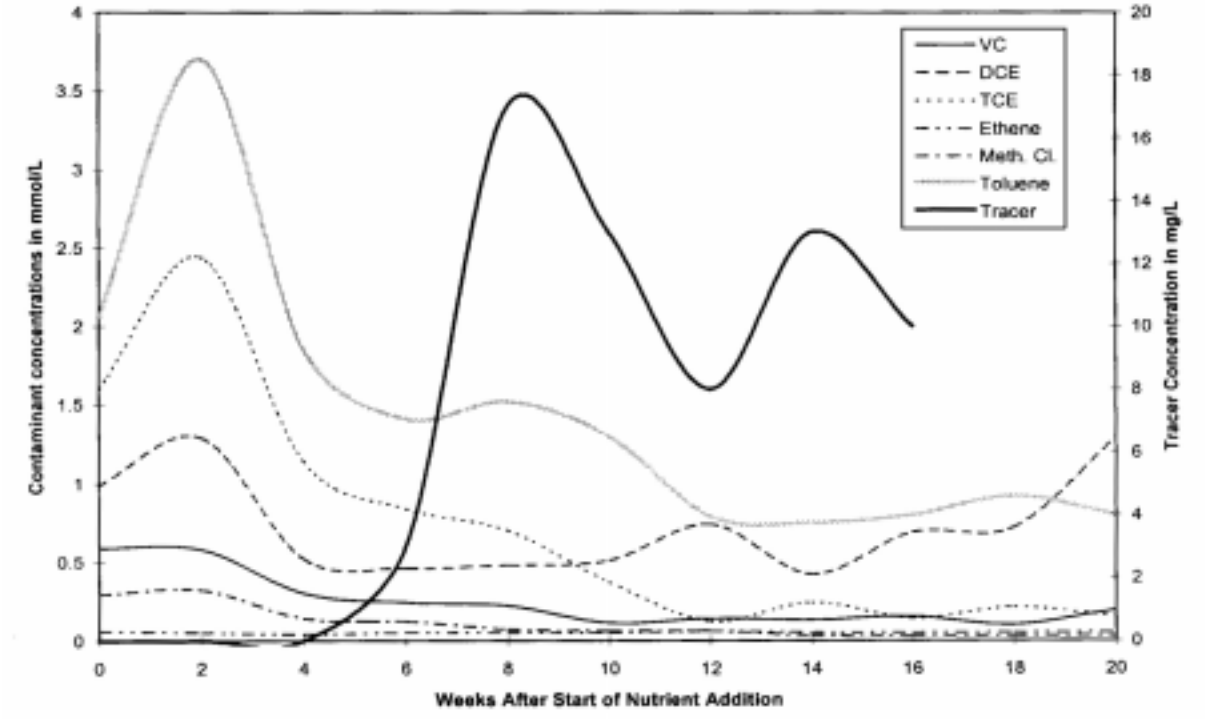


Figure 8. Contaminant monitoring data for well points 2D and 4B.

Figure 8 shows two wells, Well 2D and Well 4B, that are located in the central treatment area and provide a range of the observed monitoring well data. Well 2D is a low concentration well with very little TCE that is near the horizontal recirculation well. Nutrient arrival occurred shortly after nutrient addition as shown by the tracer concentration data measured. Well 4B has a much higher concentration of TCE and is in the lower permeability zone where nutrient breakthrough took much longer, approximately two months, and the level of nutrients delivered to this area was probably lower, as evidenced by the much lower tracer concentrations. The results for Well 2D are representative of many of the “D” level wells, showing a reduction of the chlorinated contaminants to regulatory levels in several weeks. Both DCE and vinyl chloride were reduced at a rate of 0.10-0.20 ppm per day. Since toluene was not specifically targeted for biological degradation, toluene was monitored to assess contaminant reductions attributable to mixing and redistribution. Over this period, toluene levels changed slightly while ethylene increased substantially, suggesting that anaerobic reductive dechlorination was the major mechanism for contaminant reduction. The results for Well 4B are typical of many "B” level wells, showing a much longer period for nutrient delivery and contaminant reduction than Well 2D. This is in part due to the much higher contaminant concentrations. The reductions in contaminant levels, including toluene, is similar until late in the operations where TCE continues to decrease and DCE begins to increase. The initial TCE reduction rate observed after nutrient arrival is over 2 ppm per day and as the TCE concentration approaches 0.2 mmol/L (25ppm), the degradation rate slows to 0.10-0.20 ppm per day observed in Well 2D.

In evaluating the monitoring data from all wells showing early to mid-period nutrient arrival, contaminant reduction rates of 1-2 ppm per day were observed for the high (above 200 ppm) contaminant levels to approximately 0.05-0.20 ppm per day for wells with contaminant levels of less than 20 ppm. These rates suggest that areas with moderate TCE contamination would require one to two months after nutrient arrival to reduce TCE to levels of 5-10 ppm and another one to two months to reduce the TCE to regulatory levels. The further reduction of the DCE and vinyl chloride produced to ethylene could take similar periods of time. This suggests that as much as a year may be necessary for areas of high contaminant concentration to be reduced to regulatory levels for all contaminants following nutrient availability.

Figures 9 and 10 show contaminant reduction trends by level for toluene, TCE, DCE, and vinyl chloride and the production of ethylene for the wells in the central treatment area that received nutrients. Since the monitoring points in each level do not receive nutrients at the same time, a classic step-wise dechlorination sequence was not expected. Each level was analyzed separately in an effort to identify trends in contaminant distribution and biological degradation. Similar to the results of Figure 8, contaminant reduction at each level begins as the wells receive nutrients. Level D, where most of the wells have nutrient arrival very early during system operation, is the only level where measurable ethylene production occurred. Level A, where nutrient arrival was longer, reductions in DCE and corresponding increases in vinyl chloride are observed. In Levels B and C, which have much higher contaminant concentrations and much shorter periods of nutrient availability, show much slower overall contaminant reductions. The contaminant reduction results in Levels B and C are overshadowed by the data from several monitoring points with high contaminant concentrations that had nutrient breakthrough in only the last four to five weeks of system operation. Contaminant reduction in the wells in these two levels with longer nutrient availability show more pronounced contaminant reductions as shown in Table 4.

Contaminant Reduction Levels

Thought the pilot system was not designed nor operated to meet any specific cleanup criteria during the short operational period, final contaminant levels for many monitoring points were measured below 50-100 ppb, while several of the lower concentration wells had contaminant concentrations reduced to below 5 ppb. The data also show that monitoring points with individual contaminant concentrations above 5-10 ppm were not reduced to allowable levels during the pilot operations. This data, along with the degradation rate results discussed above, suggests that though contaminant degradation is rapid once nutrients are available, the operational period of a bioremediation system could be controlled by degradation rates at the lower contaminant levels.

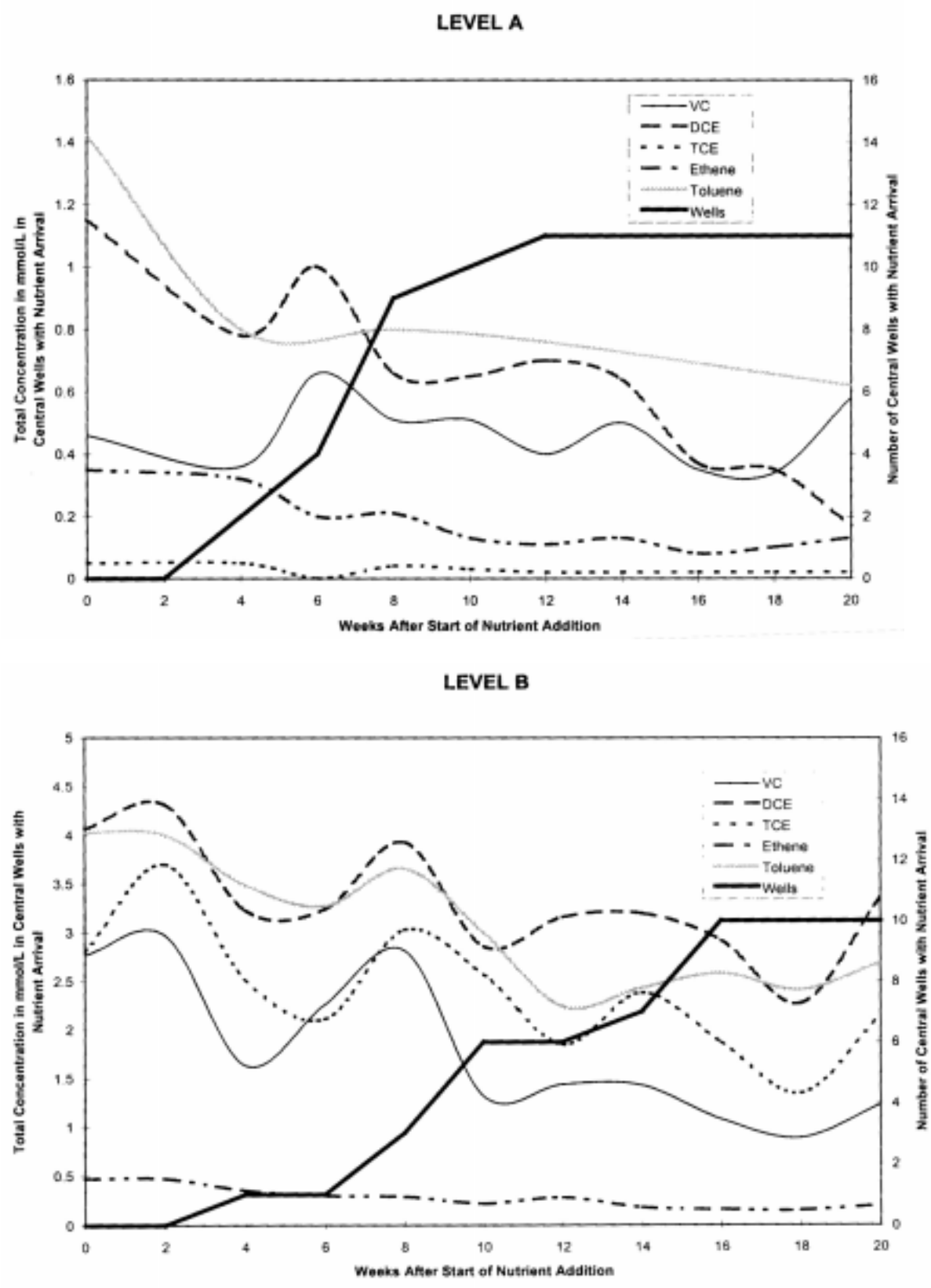


Figure 9. Contaminant monitoring data for Level A and B Wells.

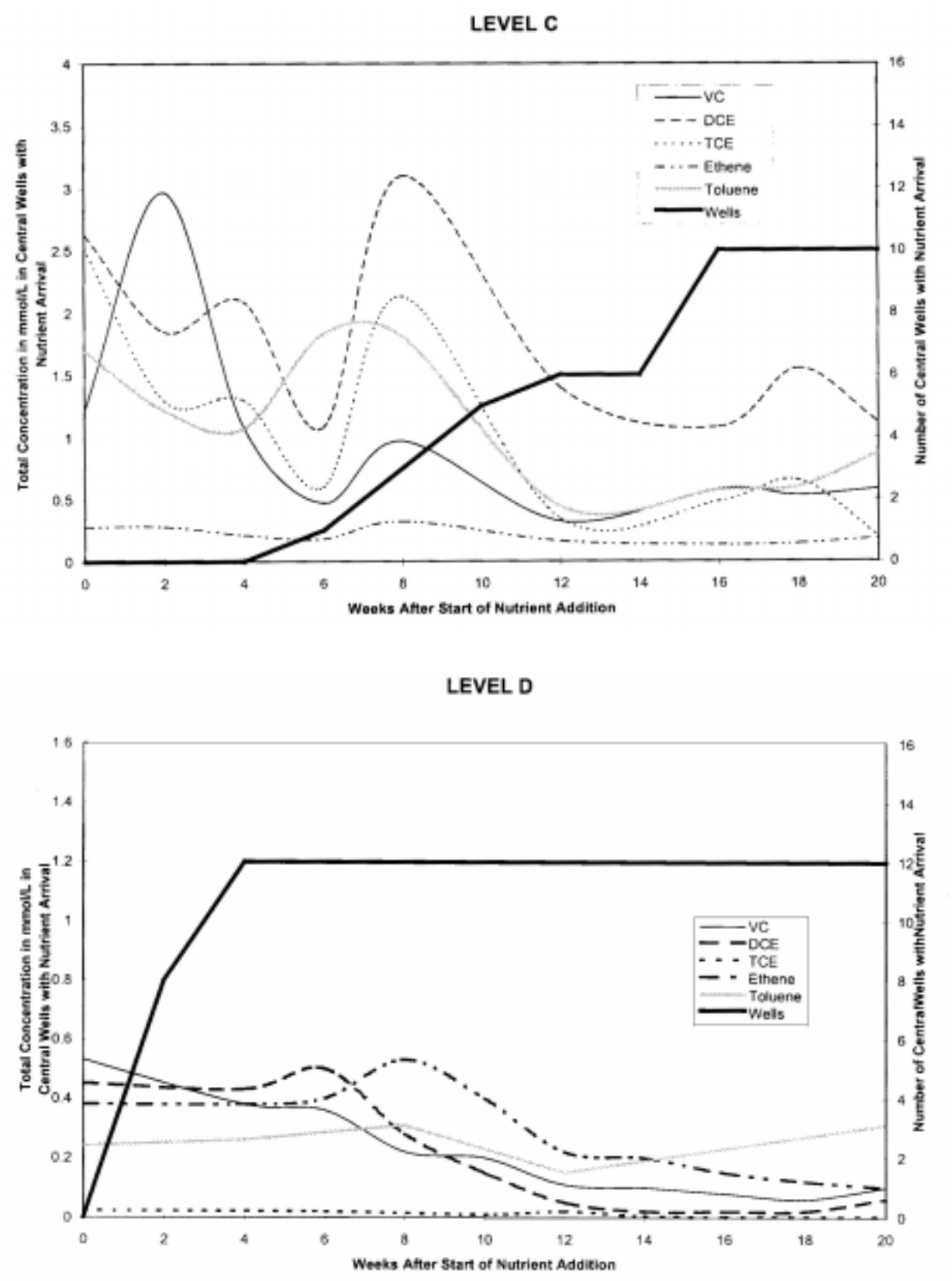


Figure 10. Contaminant monitoring data for Level C and D Wells.

Extraction Well Monitoring Data

In addition to the 64 monitoring point, the extracted ground water was monitored every two hours using an in-line, automated, gas chromatograph (GC). The system was continuously calibrated using a prepared standard. The data were compared with GC data from grab samples collected from the well. Both sets of data and were shown to be within the accuracy limits of the two instruments. The average daily data, shown in Figure 11, provide additional evidence of the biodegradation occurring in the subsurface and the overall rates of contaminant reduction. In general, the extracted ground water trends and the data from the monitoring points in the interior of the treatment zone correlate well. Contaminant reduction in the ground water began to occur rapidly in mid-April, which is the time when approximately half of the monitoring wells that would experience nutrient arrival had done so. Contaminant reduction continued throughout system operations, but was much slower as additional wells experienced nutrient arrival. The sharp increases in the contaminant concentrations and the data gaps shown for the GC generally correspond to redevelopment of the extraction well, which occurred as discussed previously on February 24, March 13, March 31, April 8, April 22, June 4, and June 16. This automated monitoring system worked well during the pilot operations and appears to be a simple method that can be used to guide operations and define sampling events of a full-scale bioremediation system.

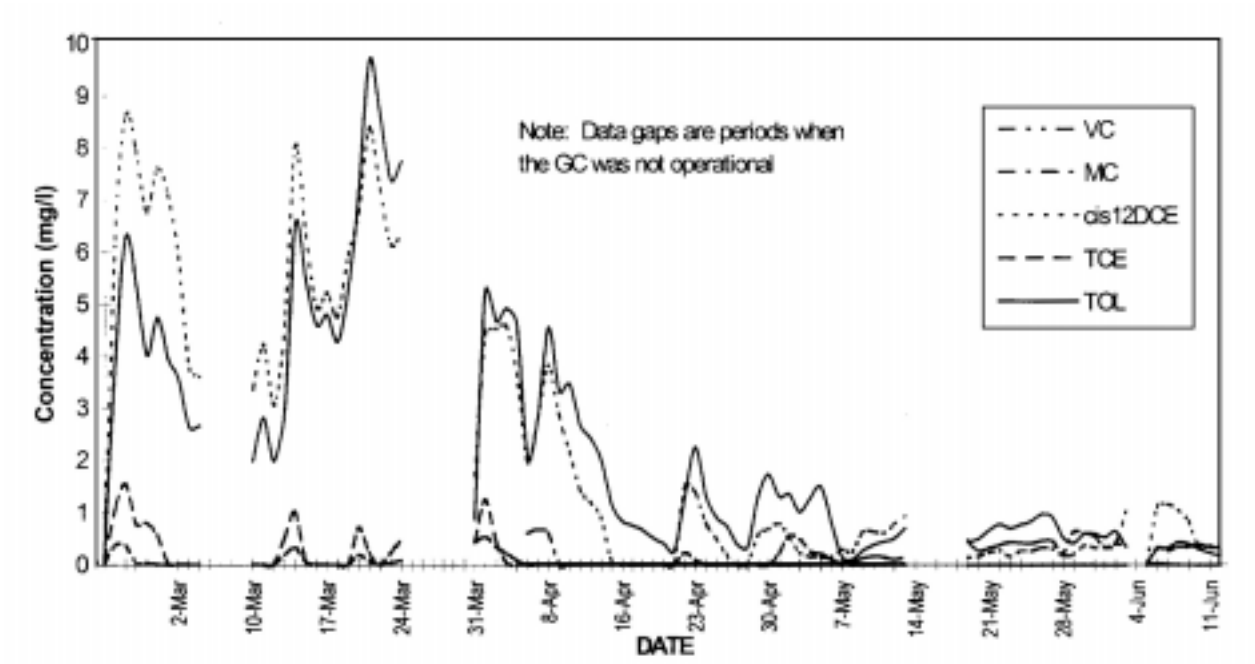


Figure 11. Continuous monitoring data of the extracted ground water.

Reduction of Other Contaminants

Table 4 and Figures 8-11 support the observation that across the site, enhanced bioremediation occurred as a result of system operations. As discussed, the pilot operations were designed to optimize conditions for the reduction of the chlorinated contaminants and were not optimized to reduce toluene. Though toluene concentrations decreased over much of the site, residual toluene levels will have to be addressed in a full-scale system design. This may require the addition of a different nutrient mix at some point during operations, though oxygen injection is often used to quickly, and effectively reduce toluene concentrations to regulatory levels.

A summary of the performance of the *in situ* anaerobic bioremediation pilot system is provided in Table 5, relative to the performance measures and objectives. Overall, the system met most of the identified system performance objectives.

Table 5. Bioremediation system performance summary.

Performance Evaluation Criteria	Values/ Results
Treatment volume:	Approximately 45 ft x 45 ft x 30 ft, 60750 ft^3
Ground water treated:	Approximately 250,000 gallons, about 2 pore volumes
Extraction/reinjection rate:	Approximately 1.5 gpm
System nutrient transport effectiveness:	Nutrients were effectively distributed to approximately 90% of the central monitoring points in 23 weeks,
Level A - 8-10 feet deep	Nutrients delivered to 88% of the monitoring points
Level B - 12-14 feet deep	Nutrients delivered to 81% of the monitoring points
Level C - 18-20 feet deep	Nutrients delivered to 81% of the monitoring points
Level D - 22-24 feet deep	Nutrients delivered to 100% of the monitoring points
Nutrient effectiveness:	Significant reductions in all contaminants occurred within 4-8 weeks after nutrient arrival at a well point
Nutrient viability	Average nutrient half-life of 110 days, up to > 1year
Contaminant degradation rates:	
>100 ppm concentration levels	1-2 ppm per day
1-10 ppm concentration levels	0.05-0.10 ppm per day
Reduction values for contaminants of concern:	
Toluene	50-70% within 4-8 weeks of nutrient arrival
TCE, DCE, vinyl chloride, methylene chloride	90–95% within 4-8 weeks of nutrient arrival
Chlorinated solvent by-product production	General decline in all contaminants with some temporary increases in degradation products, followed by reduction of the degradation products themselves by biological degradation.
Waste Generated	None, all extracted ground water was recirculated
Achievable contaminant reduction levels:	Many contaminants were reduced to the 50-100 ppb level, the detecton limit for most analyses. Some monitoring points with concentrations less than 10 ppm were reduced to <5 ppb.

6. *IN SITU* ANAEROBIC BIOREMEDIATION SYSTEM COST

The Pinellas *in situ* anaerobic bioremediation project was constructed and operated by Lockheed Martin Specialty Components (LMSC) under their cost-plus-fee management and operations (M&O) contract with DOE. Several organizations, including the EPA National Risk Management Laboratory, Sandia, FDEP, and several industry participants, played an important role in the design, operation, and monitoring of the remediation system. These services were often in an advisory or consulting role, though some direct support was provided to the project. For example, FDEP provided three-dimensional graphical data of sampling results on the Internet for use by the ITRD participants. Where appropriate, direct support costs are included in Table 6, which shows project costs in accordance with the interagency work breakdown structure adopted by the Federal Remediation Technologies Roundtable.

Table 6. Bioremediation Project cost by interagency work breakdown structure.

Cost element (with interagency WBS Level 2 code)	Description	Costs ($)	Subtotals ($)
Mobilization and preparatory work(331 01)	Four, fully-screened vertical wells at corners of treatment area	$ 10,000	$ 35,000
	Flow model calibration and analysis	$ 15,000	
	Flow meter testing	$ 10,000	
Monitoring ,sampling, testing, and analysis (331 02)	Monitoring point network	$ 15,663	$ 238,310
	Pre- and post-treatment coring	$ 20,000	
	Laboratory - VOCs (biweekly)	$ 48,728	
	Laboratory – methane, ethane, ethylene (biweekly)	$ 81,900	
	Laboratory - tracers (biweekly)	$ 9,492	
	Iodide tracer	$ 2,568	
	Laboratory - nutrients (weekly)	$ 8,860	
	Bromide tracer	$ 869	
	Labor	$ 40,230	
Ground water collection and control (331 06)	Horizontal well installation (2-240 feet long w/30 feet screens)	$ 41,235	$ 87,563
	Pumps and controls	$ 9,256	
	Trenches	$ 7,925	
	Plumbing, utilities, pad, shed, etc.	$ 29,120	
Biological Treatment (331 11)	Operations labor	$ 19,440	$ 23,748
	Methanol ~60 kg	$ 174	
	Sodium benzoate ~120 kg	$ 376	
	Sodium lactate (2 drums) ~170 kg	$ 3,483	
	Bromide	$ 869	
	Utilities: Electricity	$ 275	
General requirements (331 22)	Project management and engineering	$ 12,480	$ 12,480
		TOTAL	$ 397,074

As discussed earlier, the goal of the operation of this *in situ* anaerobic bioremediation pilot system was to assess the ability of nutrient injection to accelerate the reduction of contaminants at the Northeast Site and to identify optimum operating conditions for the design and operation of a full-scale system. Since the pilot system was not operated to meet any specific cleanup criteria and the treatment area selected had nominal contaminant levels higher than much of the Northeast Site, it would be inappropriate and possibly misleading to specify a direct treatment costs for a full-scale system implementation. However, general observations and estimates of biological treatment capital and operating costs can be made.

As can be seen from Table 6, almost two-thirds of the overall costs of the pilot operation were related to the extensive monitoring conducted. This level of monitoring was used in an effort to better understand the operation of the pilot system and to track the biodegradation occurring at different levels in the aquifer. As extensive a monitoring system and the associated costs would not be required in a full-scale system. The monitoring costs data provided though does show how systems like the continuous monitoring field GC can be used to provide significant bioremediation data at a low cost. Typical fully automated continuous monitoring systems like the one used at Pinellas are available for less than $50K.

From an operational viewpoint, the pilot system pumped approximately 250,000 gallons of water, this allowed for treatment of approximately two pore volumes of contaminated ground water in the central treatment area. The direct biological treatment costs for water treatment during the pilot operations were therefore approximately $0.10-0.12 per gallon of water treated. Since additional treatment would be required to reduce contaminants to regulatory levels in some areas, these costs are only approximate. Actual costs will vary based on the contaminant levels and the hydrogeology encountered across the site, though much of the site has significantly lower contaminant levels than the pilot study area.

The system construction, operations labor, and chemical costs are often proportional to the scale of a project and can be more easily used to quantify potential full-scale system operating and construction costs. Initial estimates of the construction and operating costs of an *in situ* anaerobic bioremediation system were developed by the ITRD Program based on site hydrogeologic data and the results of the biodegradation treatment study.[7] The initial estimates were developed by two, environmental consulting firms familiar with implementing bioremediation systems. They estimated that a vertical well based treatment system would take approximately a year to construct, require about a year to deliver nutrients to all areas of the site, and about six months to a year for contaminant degradation, for a three to four year total remediation period. The nutrient costs were estimated to be about $750K, with system operational costs of $600K per year. Capital costs for a ground water extraction and recirculation system were estimated at $2M, for an estimated total site remediation cost of $3.5-4.5M. These cost estimates assumed application of a bioremediation system in the areas of low to moderate concentration (less than 200 ppm), while the higher contaminant levels would be treated with another more aggressive technology.

The performance of the pilot system generally substantiated many of the initial performance and unit cost assumptions and related overall cost estimates. Based on the pilot data, it appears that it would take about 6-8 months to get nutrients to all levels of the aquifer and another 8-12 months for contaminant degradation and reduction in all levels to regulatory limits, or about two years for system operations. Based on nutrient costs and the levels used for the pilot and two year operational period, nutrient costs for treatment of the three to four-acre Northeast Site would be about $750K to $1M, depending on the savings of buying nutrients in bulk quantities. Scaling of the construction costs of the horizontal pilot-system for application to the entire Northeast Site suggest a full-scale cost of approximately $3-4M. These results suggest that a full-scale bioremediation system based on a horizontal extraction and recirculation design would cost $4.5-5.5M to construct and operate for a two to three-year period. The required operational period and associated costs for some portions of the system might be reduced since much of the Northeast Site has nominal contaminant levels of 10-30 ppm, rather than the higher contaminant levels observed in the selected pilot-system treatment area.

7. REGULATORY/INSTITUTIONAL ISSUES

In July 1993, DOE, EPA, FDEP, and LMSC entered into an agreement with the ITRD Program to evaluate innovative technologies to remediate ground water contamination at the Pinellas STAR Center Northeast Site effectively and expeditiously.

Under Section II.D.1 of the Department of Energy's HSWA Permit, interim measures may be conducted at SWMUs after EPA approval. Section II.D.3 requires the permittee to notify the EPA Regional Administrator, as soon as possible, of any planned changes, reductions, or additions to the interim measures. The proposed *in situ* anaerobic bioremediation project would temporarily interrupt the operation of the existing interim measures (pump and treat with air stripping); therefore, the DOE provided notice to the EPA and FDEP of a planned change (the implementation of ITRD field activities) to the approved interim measures and proposed implementation schedule for concurrence in August 1996. Authorization for implementation of the activities was received in August 1996.

Initially, both industry and regulatory participants of the ITRD committee were concerned that underground injection control (UIC) requirements may prevent the recirculation of ground water. Through assistance from the FDEP, discussions were held with the State of Florida, who has UIC delegation, about this issue. Because of the system design (i.e., *in situ* recirculation) the state determined that no UIC permit was required.

8. SCHEDULE

Figure 12 shows the tasks and schedule associated with the *in situ* anaerobic bioremediation project at the Pinellas STAR Center.

ID	Task Name	Start	Finish
1	Workplan completed	8/1/96	8/1/96
2	System construction	8/1/96	11/8/96
3	Install horizontal wells	8/19/96	8/22/96
4	Install infiltration trenches	9/3/96	9/17/96
5	Install monitoring network	9/26/96	10/1/96
6	System checkout & hydraulic tests	10/1/96	12/20/96
7	System operation	2/10/97	6/27/97
8	Recirculate ground water	2/10/97	6/27/97
9	Add methanol & benzoate	2/12/97	6/27/97
10	Add lactate	2/27/97	6/23/97
11	Conduct tracer study	3/7/97	6/4/97
12	Add iodide to trenches	3/7/97	6/4/97
13	Add bromide to lower horiz well	3/7/97	4/25/97
14	Groundwater sampling	11/7/96	7/9/97
15	Pretreatment VOC sampling	11/7/96	11/8/96
16	Operational VOC sampling	2/17/97	7/8/97
17	Methane, Ethane, Ethene sampl	3/4/97	7/9/97
18	Tracer sampling	3/7/97	7/7/97
19	Nutrient sampling	5/8/97	7/9/97

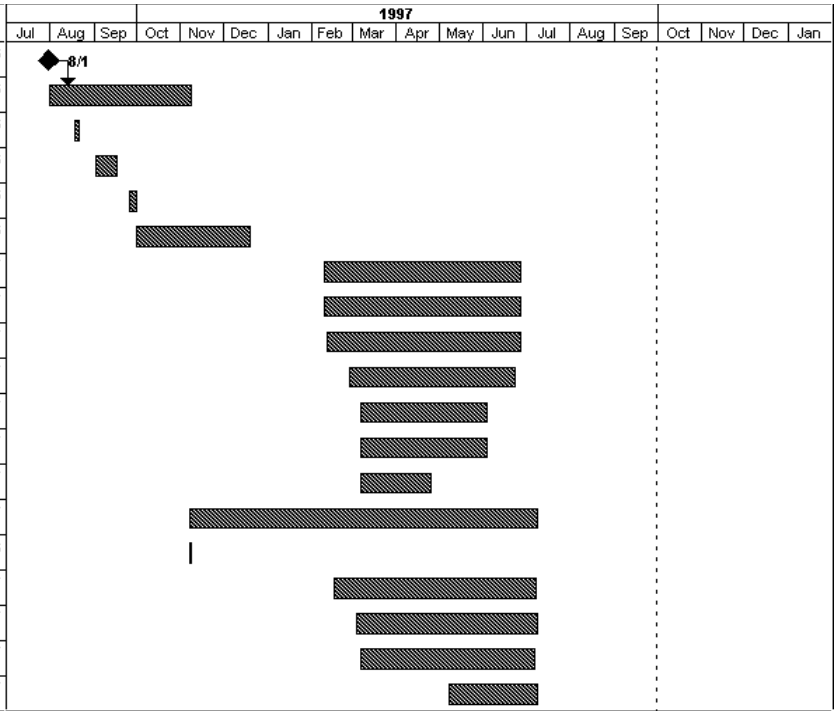


Figure 12**. Bioremediation project schedule.**

9. OBSERVATIONS AND LESSONS LEARNED

Cost Observations and Lessons Learned

Based on the construction and operating treatment cost data from the pilot system operation, it appears that *in situ* anaerobic bioremediation is a cost-effective method for reducing chlorinated VOCs in subsurface environments, given favorable geochemical, microbal, and hydraulic/hydrologic characteristics, such as at the Pinellas Northeast Site.

Performance Observations and Lessons Learned

Laboratory batch and column studies, using site soil and ground water, if used correctly can help identify whether a population of anaerobic microorganisms exists capable of remediating the contaminants of concern at a site and which nutrients can enhance degradation of those contaminants.

Good nutrient distribution is critical to effectively enhancing contaminant degradation in a treatment area. Therefore, a thorough and detailed understanding of the site hydrology is necessary to design an effective nutrient delivery system. Flow meter field testing and numerical modeling should be used to help identify the best nutrient delivery system for a site.

The recirculation system of infiltration trenches and two horizontal wells developed for this site proved effective in the pilot operations. Because of the recirculation design, no waste water was generated. Improvements, such as deeper surface trenches and the flexibility of switching extraction and injection roles of the horizontal wells, could accelerate nutrient delivery to the middle and lower permeability layers and overall remediation of the site. Effective redevelopment of long horizontal wells can sometimes be difficult and should be considered in the overall design and operation of a full-scale system.

At monitoring points were nutrient breakthrough was observed for at least four to eight weeks, significant declines in total chlorinated VOC concentrations (70-95%) were generally observed. These values correlate well with the results from the extraction well. For those wells where nutrient arrival was not observed, generally in the areas of lower permeability or in perimeter wells, only modest contaminant reductions were recorded. Though the nutrient mixture and concentrations were not specifically optimized during pilot operations, degradation rates as high as 1-2 ppm per day were observed in higher concentration areas (>100 ppm), while in areas with lower concentrations degradation rates ranging from 0.05 to 0.10 ppm per day were observed. It is possible that the nutrient mixture might be adjusted to further accelerate contaminant reduction. There was little evidence of significant degradation product buildup at monitoring wells after nutrient arrival.

Contaminant degradation observed in the pilot study at concentrations higher than 200 ppm suggests that anaerobic bioremediation is more robust and has a broader operational capability than previously identified.

Summary

The extensive modeling and hydrogeologic, nutrient transport, and operating cost data developed during the pilot system operation suggest that nutrient addition to stimulate *in situ* anaerobic biological degradation of chlorinated solvent contaminated soil and ground water is a feasible, cost-effective, remediation approach at the Pinellas Northeast Site for areas of moderate contamination. The limiting factors for successful, cost-effective implementation are the ability to deliver appropriate nutrients to all contaminated areas and hydraulic travel times.

10. REFERENCES

1. *Installation Assessment, Pinellas Plant*, U.S. Department of Energy, Comprehensive Environmental Assessment and Response Program, Albuquerque Operations Office, Albuquerque, N.M., 1987.

2. *RCRA Facility Investigation Report, Pinellas Plant*, U.S. Department of Energy, Environmental Restoration Program, Albuquerque Operations Office, Albuquerque, N. M., 1991.

3. *RCRA Hazardous and Solid Waste Amendments Permit, U. S. Department of Energy Pinellas Plant, Largo, Florida.* EPA ID No. FL6-890-090-008, U.S. Environmental Protection Agency, February 9, 1990.

4. *Interim Corrective Measures Study, Northeast Site*, TPA2 6350.80.01, prepared by CH2M Hill for the U.S. Department of Energy and General Electric Company, Neutron Devices Department, Largo, FL, May 1991.

5. *Corrective Measures Study Report, Northeast Site, Pinellas Plant, Largo, Florida*, U.S. Department of Energy, Environmental Restoration Program, Albuquerque Field Office, Albuquerque, N.M., 1993.

6. Flanagan, W.P., et al. “Anaerobic Microbial Transformation of Trichloroethylene and Methylene Chloride in Pinellas Soil and Ground Water,” General Electric Corporate Research and Development Center, Schenectady, NY, May 1995.

7. Pinellas Northeast Site Project, Innovative Technology Review, letter to David Ingle, U. S. Department of Energy, from Mike Hightower, Sandia National Laboratories, February 8, 1995.

11. VALIDATION

Signatories:

"This analysis accurately reflects the performance and costs of the remediation."

David S. Ingle, ER Program Manager
U.S. Department of Energy
Grand Junction Office

Mike Hightower, Technical Coordinator
Innovative Treatment Remediation Demonstration Program
Sandia National Laboratories

Guy Sewell, Research Microbiologist
National Risk Management Research Laboratory
U.S. Environmental Protection Agency

Department of Environmental Protection

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2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Virginia B. Wetherell
Secretary

April 14, 1998

Mr. David Ingle
c/o MACTEC-ERS
7887 Brian Dairy Road
Suite 200
Largo, Florida 33777

Dear Mr. Ingle:

I have reviewed the "Cost and Performance Report, In Situ Anaerobic Bioremediation, Pinellas Plant Northeast Site" final draft dated March 16, 1998. I concur with the purpose of the report. Unless the EPA or other parties desire modifications, we recommend that the report proceed to "final" designation.

If I can be of any further assistance with this matter, please do not hesitate to contact me at 904/921-9983.

Sincerely,

John R. Armstrong P.G.
Remedial Project Manager

April 14, 1998
Date

CC: Cheryl Walker-Smith, USEPA Atlanta
Satish Kastury, FDEP

JJC JJR ESN ESN

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4
ATLANTA FEDERAL CENTER
61 FORSYTH STREET, SW
ATLANTA, GEORGIA 30303-8909

APR 28 1998

4WD-FFB

CERTIFIED MAIL
RETURN RECEIPT REQUESTED

The United States Department of Energy
Pinellas Plant
ATTN: Mr. David Ingle
P.O. Box 2900
Largo, FL 34649

SUBJ: Revised Cost and Performance Report: In Situ Anaerobic Bioremediation
Pinellas Northeast Site, Largo, Florida
Final Draft - March 16, 1998
DOE Pinellas Plant, FL
EPA I.D. Number FL6 890 090 008

Dear Mr. Ingle:

The Environmental Protection Agency (EPA), Region 4, has completed our review of the revised Cost and Performance Report for the in situ anaerobic Bioremediation project conducted at the Northeast Site (Solid Waste Management Unit PIN 15). This work was conducted under the Innovative Treatment Remediation Demonstration (ITRD) agreement between EPA Region 4, the Florida Department of Environmental Protection (FDEP), the U.S. Department of Energy, Clean Sites, Inc., the EPA Technology Innovation Office, and Sandia National Laboratories. This team's mission was to identify and demonstrate various innovative technologies applicable to this and other contaminated waste sites around the country. This is the third innovative technology demonstration conducted at the Northeast Site.

This project utilized the experience and expertise of personnel from the EPA National Risk Management Research Laboratory (NRMRL) and Lockheed-Martin in the design, construction, implementation, and sampling efforts. The FDEP participants played a key role in system design, permitting issues, and computer support. The facilitator of the ITRD effort, Mr. Mike Hightower, deserves special credit for unifying and focusing the efforts of this team, and in the overall success of this ITRD project.

The EPA approves of the changes made in this revised document and looks forward to the possibility of other ITRD projects occurring across Region 4.

Any and all concerns raised by the FDEP for this revised document must be addressed as required under their authority.

Sincerely,

Carl R. Froede Jr.

Carl R. Froede Jr., P.G.
DOE Remedial Section
Federal Facilities Branch
Waste Management Division

cc: J. Crane, FDEP
E. Nuzie, FDEP
J. Armstrong, FDEP